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Effect of Steric Hindrance on Desorption Processes of Alkanethiols on Au(111)

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Thermal decomposition processes of self-assembled monolayers (SAMs) on Au(111) composed of various thiol molecules were explored by thermal desorption spectroscopy (TDS). Desorption as disulfides was always observed for the methanethiol SAMs at any coverage, whereas the desorbed species from the SAMs of *n*-octanethiol strongly depended on the molecular density. In the case of cyclohexanethiol (cyclohexyl mercaptan), only monomers (thiol) desorbed from the SAM. In the cases of the mixed SAMs comprised of cyclohexylthiol and other thiolates (methanethiol and octanethiol), the desorption of asymmetric disulfides in a small yield was observed. TDS and X-ray photoelectron spectroscopy measurements revealed that these thiols are chemically bound to gold surfaces and that there was no significant difference in the chemical characters of their bonds to the substrates. These results suggest that the structure of a thiol molecule plays a critical role in determining the manner of desorption, thus providing hints for improving the thermal stability of SAMs.

Introduction

Self-assembled monolayers (SAMs) of thiol families on gold substrates have long attracted much attention due to their ease of preparation and their high ordering. For decades, SAMs have played an important role as model systems for a variety of practical applications including biosensors and molecular electric devices.^{1,2} In these applications, the stability of the monolayers is critical, since the devices are sometimes required to work under harsh conditions, such as exposure to high temperatures, corrosive solutions, and oxidation. The thermal stability of SAMs is an important issue affecting their suitability for practical applications. Although the thermal desorption processes of the SAMs have been investigated with various techniques,^{3–14} several fundamental questions still remain unsolved. One of them is the factor governing the desorption behavior of molecules. The SAMs prepared with *n*-alkanethiols at room temperature show a two-step desorption; i.e., the disulfide molecules first desorb at 350–450 K, and the thiolate molecules then desorb at 400–500 K.^{8,13,14} Although there has been good consensus in the reports regarding the desorption processes, the underlying mechanism has still not been fully clarified.

Several factors have been reported to govern the desorption processes of the molecules constituting the SAMs. These factors include molecular length,⁷ molecular structures,^{7,15} surface roughness,¹⁶ the temperature of the substrate during the adsorption of thiols,⁶ etc. In this work, we focused on the effects of molecular structures on the manner of desorption and investigated the desorption processes of normal alkanethiols with different lengths of alkyl chains and cyclohexanethiol (cyclohexyl mercaptan) molecules along with comparing their chemical adsorption states as characterized by X-ray photoelectron spectroscopy (XPS).

Experimental Section

Au(111) substrates were prepared by vacuum deposition of gold onto freshly cleaved mica (10 × 10 × 0.3 mm, S&J TRADING INC.) at 620 K under a vacuum pressure of 10^{-5} – 10^{-6} Pa. The substrates were then annealed at 620 K in a vacuum chamber for 2 h. Dimethyldisulfide (C1), *n*-octanethiol (C8), and cyclohexanethiol (CHT) were purchased from Aldrich Chemical Co. and used without further purification. The monolayers of these thiol derivatives were formed by dipping Au(111) substrates into freshly prepared ethanolic solutions containing the corresponding compounds at a concentration of 1 mM for 24 h. To prepare SAMs composed of two thiols (disulfides), we simply prepared the mixture of the corresponding solutions (1 mM) at a 1:1 ratio and immersed the Au substrates into the mixed solution for 24 h. After immersion, the samples were carefully rinsed with pure ethanol to remove physisorbed molecules from the surface.

TDS measurements were carried out in an ultrahigh vacuum chamber (5×10^{-8} Pa) with a quadrupole mass spectrometer (QMG-421, Balzers, Liechtenstein). The heating ratio was 1 K/s. The surface temperature was measured by a chromel–alumel thermocouple in tight contact with the sample. The pressure in the chamber was increased up to $\sim 10^{-6}$ Pa during the measurements.

The adsorption states of the thiolates (S_{2p} states) were characterized by XPS (Theta Probe, Thermo Fisher Scientific, U.K.). Al K α radiation (photon energy of 1486.6 eV and spot size of 400 μ m) was used for the x-ray. The pass energy of the analyzer was fixed at 100 eV. The base pressure of the measurement chamber was below 2×10^{-7} Pa. We calibrated the binding energies against the $Au_{4f5/2}$ peak (87.6 eV).

The structures of the molecules on the substrates were observed with a scanning tunneling microscope (STM) (NanoScope IV, Veeco Inc., Santa Barbara, CA) and a commercially available Pt/Ir tip (80:20). All STM images were obtained in air using a constant current mode at room temperature. The bias

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voltage and tunneling current were fixed at 500 mV and 300 pA, respectively.

Results and Discussion

Figure 1a shows the TD spectra of desorbed species from the C8 SAM at its saturated coverage. The desorbed species and temperatures for their desorption are summarized in Table 1. First, species with $m/e = 290$ desorbed at around 380 K, followed by the desorption of species with $m/e = 145$ at 448 K and the species with $m/e = 146$ at 456 K. These species with $m/e = 145$, 146, and 290 are assigned to a C8 thiolate radical [$\text{CH}_3(\text{CH}_2)_7\text{S}$], C8 thiol [$\text{CH}_3(\text{CH}_2)_7\text{SH}$], and C8 disulfide [$\text{CH}_3(\text{CH}_2)_7\text{SS}(\text{CH}_2)_7\text{CH}_3$], respectively (Table 1). The trend of the data points for the C8 thiolate has almost perfect coincidence with that of the C8 disulfide in the region of 350–400 K (the time difference in sampling these masses was approximately 0.1 s). Therefore, a small peak of C8 thiolate at 380 K can be attributed to the fragmentation of the C8 disulfide decomposed in the mass spectrometer. The production of C8 thiols is explained by the hydrogen abstraction of C8 thiolate from the wall inside the chamber, as has already been reported in previous studies.^{14,17,18} Since normal alkanethiols are considered to be adsorbed on Au(111) surfaces as thiolate molecules after the cleavage of S–H bonds when the monolayer is prepared at room temperature,^{11,19} the hypothesized desorption of the C8 disulfide and thiolate from the SAM appears reasonable and consistent with the desorption manner of other normal alkanethiols.^{8,13,14}

In order to identify the desorption species from the C8 SAM with low molecular density, we performed the following measurement. The sample was heated to 420 K (temperature for the desorption of the C8 disulfide) and maintained there for 60 s. We then performed a TDS measurement after cooling down to room temperature. Figure 1b shows the TD spectra of the C8 SAM after heating. Unlike the desorption process at saturated coverage, as shown in Figure 1a, the desorption peak of C8 disulfide was not observed. After the heating at 420 K (the first heating), we performed STM measurements and observed the flat-lying structure (striped phase) (Figure 1c). In this structure, the C–C–C plane of the alkyl chains the C8 thiolates is parallel to the surface.²⁰ In this structure ($11.5 \times \sqrt{3}$ structure), the density is estimated to be approximately 25% of the density of the stand-up phase at its saturated coverage. The distances between the lines of bright spots, which are considered as sulfur atoms, are about 3.5 nm. This indicates that the molecules adopt the head-to-head configuration. Our results show that the desorption from the C8 SAM critically depends on the molecular density and structures, in good agreement with the report by Kondoh et al., who found that the structures of the hexanethiol SAM on Au(111) govern the desorption manner (monomer or dimer); i.e., only thiolate molecules (monomers) desorb from a low-density phase (flat-lying phase), while disulfide molecules (dimers) desorb from a high-density phase (stand-up phase).^{13,14}

We also carried out the same measurement for the C1 SAM to investigate the effect of an alkyl chain. First, we performed STM measurements of the C1 SAM at its saturated coverage and found etch pits formed on the substrate, indicating the strong interaction of their sulfur head groups with substrates.²¹ Figure 2a shows the TD spectra of the C1 SAM at its saturated coverage. The C1 disulfide (CH_3SSCH_3 , $m/e = 94$) and its fragments, which are C1 thiolate radicals (CH_3S , $m/e = 47$) and C1 thiols (CH_3SH , $m/e = 48$), were also observed at 364 K. The desorption of the C1 thiolate radical and the C1 thiol was observed at 448 K. This process is the same as that for the

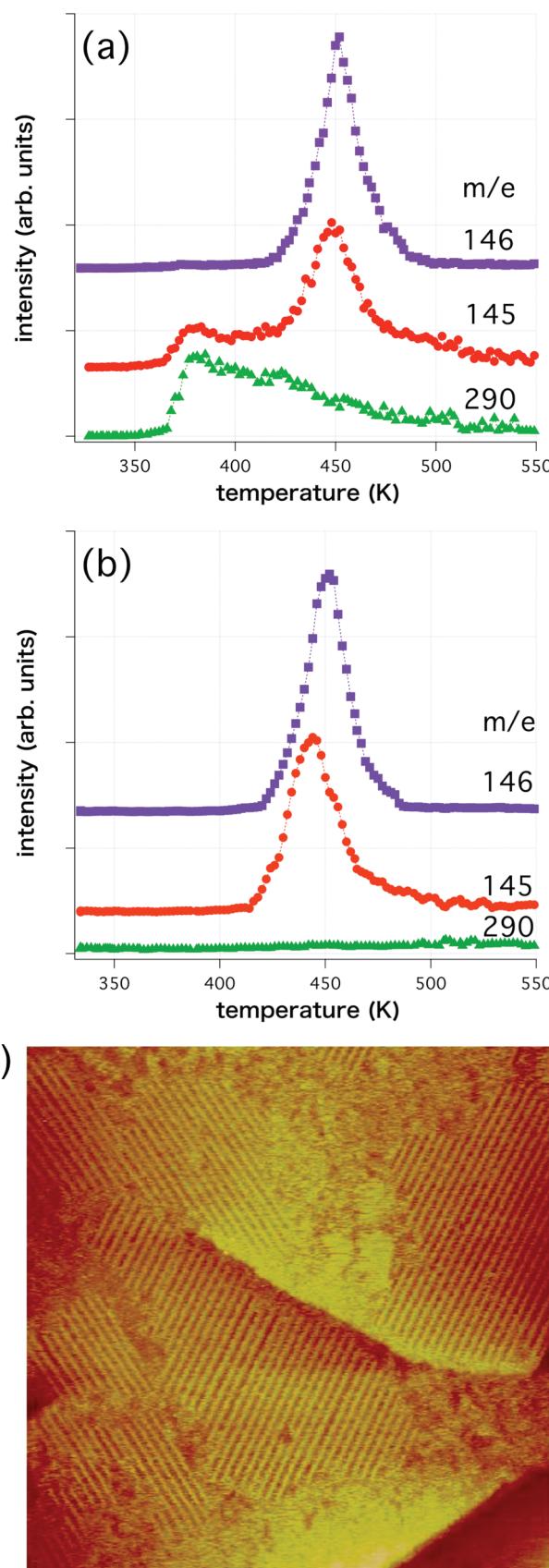


Figure 1. Thermal desorption spectra of the C8 SAM (a) after preparation and (b) after heating at 420 K for 60 s ($m/e = 146$, C8-S^+ ; $m/e = 145$, C8-S^+ , C8-SS-C8^{+2} ; and $m/e = 290$, C8-SS-C8^+). (c) STM image (15×15 nm) of C8 SAM taken in air after heating at 420 K for 60 s in ultrahigh vacuum. The bias voltage and tunneling current were fixed at 500 mV and 300 pA, respectively.

TABLE 1: Desorbed Species from the SAMs Studied in This Work and Temperatures of Each Desorption Peak

SAM	desorbed species (<i>m/e</i>)	peak temperature, K
C8	C8 thiol (146)	456
	C8 thiolate (145)	448
	C8 disulfide (290)	381
C8 (low coverage)	C8 thiol (146)	452
	C8 thiolate (145)	444
C1	C1 thiol (48)	448
	C1 thiolate (47)	448
	C1 disulfide (94)	364
C1 (low coverage)	C1 thiol (48)	452
	C1 thiolate (47)	452
	C1 disulfide (94)	412
CHT	CH thiol (116)	419
	CH thiolate (115) ^a	419
	CH disulfide (230) ^a	391
C1-CHT	C1 thiol (48)	438
	C1 thiolate (47)	438
	C1 disulfide (94)	364
	CH thiol (116)	428
	C1-CHT disulfide (162)	364 ^b
C8-CHT	C8 thiol (146)	440
	C8 thiolate (145)	437
	C8 disulfide (290)	367 ^b
	CH thiol (116)	427
	C8-CHT disulfide (260)	370 ^b

^a Very weak. ^b Very broad.

C8 SAM. We also investigated the desorption process for the C1 SAM with a low molecular density using the same heating procedure as that for the C8 SAM. As shown in Figure 2b, in addition to desorption of the C1 thiol and thiolate, the C1 disulfide desorption was also observed. There is a difference in the peak positions of the desorption of the C1 disulfide (Table 1), indicating that the desorption of the C1 disulfide is second-order desorption and thus that the molecules are adsorbed dissociatively, consistent with previous vibrational spectroscopic works.^{19,22}

We next discuss the temperatures of the desorption peaks for disulfides and thiolate radicals in the cases of the C1 and C8 SAMs (see Table 1). The desorption temperature (peak top) of the C8 disulfide is 17 K higher than that of the C1 disulfide. The C1 and C8 SAMs are known to form a structure of $\sqrt{3} \times \sqrt{3}R30^\circ$ and $c(4\sqrt{3} \times 2\sqrt{3})$, which is a superstructure of $\sqrt{3} \times \sqrt{3}R30^\circ$, respectively, and their molecular densities on the substrates are equivalent.^{23,24} Therefore, intermolecular interactions due to van der Waals interactions are a factor in governing the activation energy for desorption. The difference in the intermolecular interaction energy between these SAMs is estimated to be 48 kJ/mol,^{14,25} rationalizing the difference in the desorption temperature of these disulfides.

In contrast to the temperatures for disulfide desorption, the temperatures for the desorption of the thiolate radicals are nearly the same (448 K), indicating that there is no effect of chain length on the desorption energy of the thiolate radicals. Wetterer et al. have reported that the activation energy for the desorption of *n*-alkanes from a metal surface correlates linearly with the chain length of the molecule.²⁶ If thiolate molecules in the C8 SAMs at low coverage still take on the flat-lying configuration at elevated temperature, the C1 and C8 thiolates differ in activation energies for desorption due to the difference in the length of the alkyl chains. The difference is estimated to be 50–60 kJ/mol,²⁶ which may result in a noticeable difference in the desorption temperature of the thiolate radicals. From the above discussion, we conclude that there is a small interaction between the alkyl chains and substrate due to the thermally activated flopping motion of the alkyl chains at

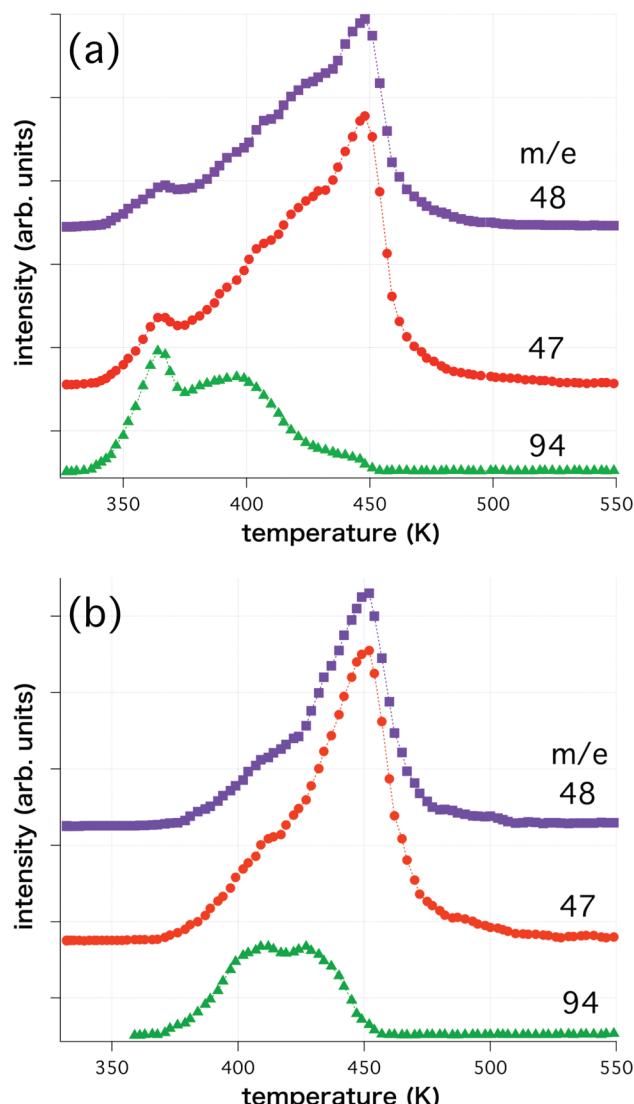


Figure 2. Thermal desorption spectra of the C1-SAM (a) after preparation and (b) after heating at 420 K for 60 s (*m/e* = 48, C1-SH⁺; *m/e* = 47, C1-S⁺, C1-SS-C1²⁺; and *m/e* = 94, C1-SS-C1⁺).

the temperature for the desorption of the thiolates, which is much higher than the temperature for the desorption of *n*-alkanes. In such a situation, the Au–S bonds do govern the temperature for the desorption of thiolate radicals.

Next, we switch our discussion to the chemical characters of Au–S bonds. Parts a and b of Figure 3 show the XP spectra of C1- and C8-SAMs at different coverages prepared by the same procedure described above. Our peak fitting revealed that two dominant peaks exist at 162.1 and 163.2 eV in the S 2p region. These peaks are widely known as bound S states, which show doublet structure of S_{2p3/2} and S_{2p1/2}, respectively.^{27,28} This doublet should be the structural unit of a fit, if several different chemical species are involved. In addition, an unbound state, which was observed for powder of alkanethiol, was also found at around 164.5 eV with minor population (less than 5%) with respect to the total peak area. The XP spectra designate that the C1 and C8 thiolates have both dominant bound and minor unbound states at high and low coverages. This result indicates that the chemical characters of Au–S bonds of the C1- and C8-thiolates are similar at both high and low coverages. Accordingly, we concluded that the character of the Au–S bonds is not a major factor in determining the desorption manner in the cases of the C1- and C8-SAMs.²⁹

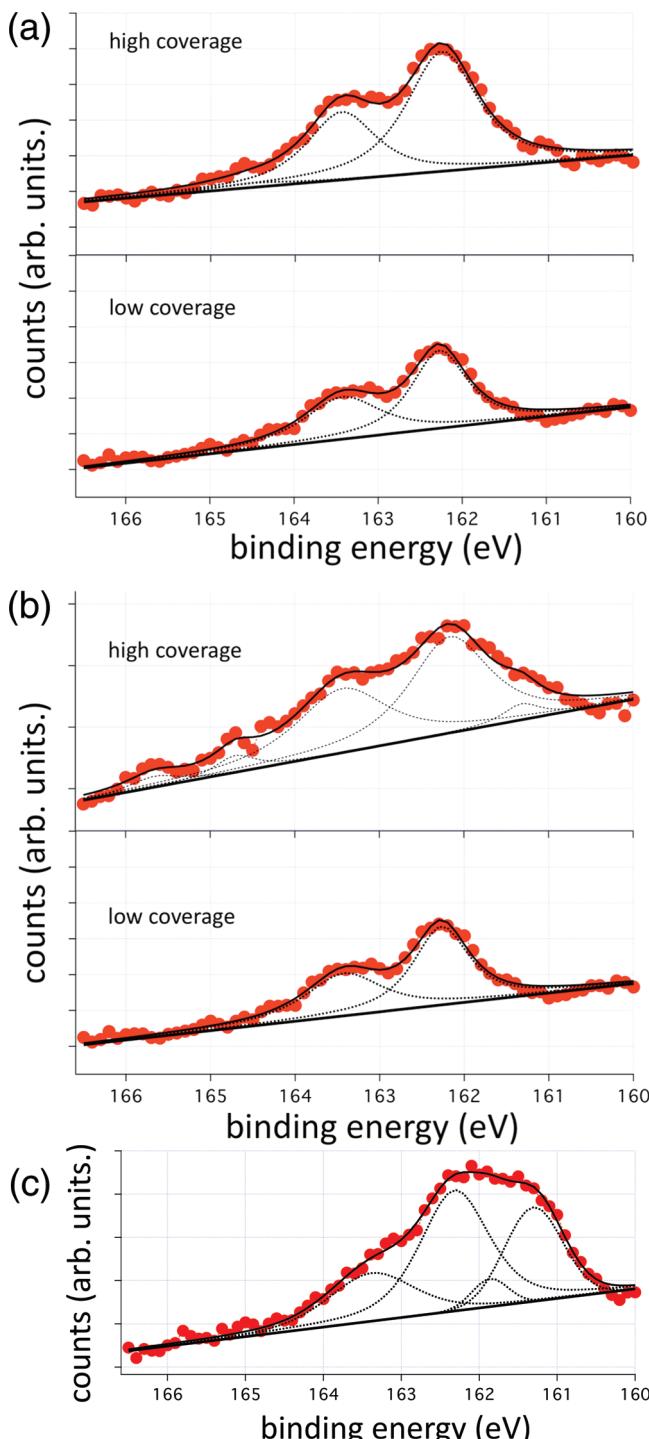


Figure 3. XP spectra and results of fitting to them in the S 2p region for (a) C1 SAM, (b) C8 SAM with different coverages, and (c) CHT SAM at its saturated coverage. The SAMs with a low coverage were prepared by heating at 420 K for 60 s under UHV.

On the basis of these results, we propose a model for the thermal desorption process of the C1 and C8 SAMs. For the C8 SAM at saturated coverage, the molecules are densely packed, and they can easily approach each other to dimerize with elevating temperature. However, when the coverage of the C8 SAM is decreased, the adsorbed molecules cannot approach each other because of the steric hindrance of the alkyl chain, resulting in a low probability for the dimerization. In contrast to the C8 SAM, the C1 molecules can approach each other at any coverage because of their small steric hindrance.

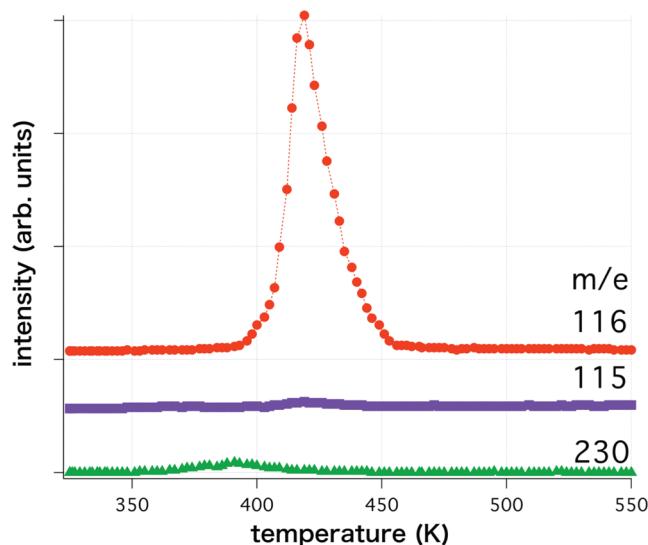


Figure 4. Thermal desorption spectra of the CHT SAM ($m/e = 115$, CH-S⁺ and $m/e = 230$, CH-SS-CH⁺).

To acquire further information regarding the effects of steric hindrance of the thiol molecules on the desorption process, we investigated the desorption species from the CHT SAM. Figure 4 shows TD spectra of the CHT SAM. The CH thiol ($m/e = 116$) exhibited a desorption peak at 419 K, while the desorption peak of the disulfides ($m/e = 230$) was very tiny. Note that the desorption of the CH thiolate was not observed, suggesting that the molecules are adsorbed as thiols. However, Kodama et al. have reported that SH bonds of alkanethiols (*n*-hexanethiol in their case) are cleaved at around 280 K and that physisorbed thiols desorb at 250–300 K based on the results of TDS. By fitting the XP spectrum of CHT SAM in Figure 3, four peaks at 161.3, 161.9, 162.4, and 163.3 eV were found to be dominant, and they are identified as bound S 2p states with various (at least two) adsorption states probably due to the effect of the bulky structure of CHT molecule on the configuration of the Au–S bonds, whereas unbound S 2p states were not observed in the region of 164–166 eV.

The XPS and TDS results indicated that CH thiols are strongly chemisorbed on Au(111) surfaces; i.e., the CHT molecules can be expected to adsorb on gold as a thiolate. Moreover, we measured a vibrational spectrum of CHT SAM by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and found no peak assigned to the SH stretching mode. The origin of the formation of the CH thiol might be due to recombination of the CH thiolate and hydrogen atom, which originated from the thermal decomposition of the CHT molecules during heating, as we observed the strong fragmentation of the CHT molecules above 375 K.

What is the factor that inhibits the dimerization of the CH thiol (or thiolate) molecules? The structure of CHT SAM was previously studied by Noh et al. by using an STM.³⁰ They reported that the molecules formed a highly ordered structure with an average area per molecule of 88.3 Å²/molecule, which is significantly larger than that for *n*-alkanethiol (21.6 Å²/molecule). The difference obviously originates from the molecular structures of the molecules. Therefore, the steric hindrance can be considered as a likely factor suppressing the dimerization.

To confirm the above assumption, the desorption behavior of molecules from mixed SAMs composed of two thiols (C1-CHT and C8-CHT) was investigated.^{31–33} The TD spectra in Figure 5a indicate that the C1 thiolate, the C1 disulfide, and the asymmetric C1-CHT dimer desorbed at 360–380 K and

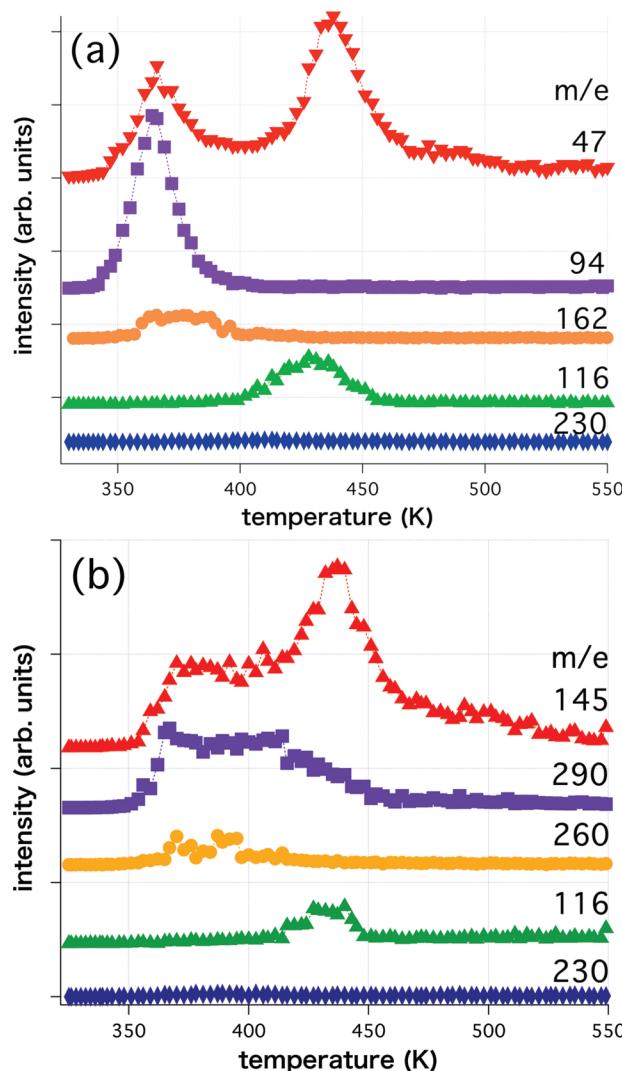


Figure 5. (a) Thermal desorption spectra of the mixed SAM of C1 and CH thiol ($m/e = 47$, $C1-S^+$; $m/e = 94$, $C1-SS-C1^+$; $m/e = 115$, $CH-S^+$; $m/e = 230$, $CH-SS-CH^+$; and $m/e = 162$, $C1-SS-CH^+$). (b) Thermal desorption spectra of the mixed SAM of C8 and CH thiol ($m/e = 145$, $C8-S^+$; $m/e = 290$, $C8-SS-C8^+$; $m/e = 115$, $CH-S^+$; $m/e = 230$, $CH-SS-CH^+$; and $m/e = 260$, $C8-SS-CH^+$).

that the desorptions of the C1 and CH thiolate molecules were detected at around 430 K. We also confirmed that there was almost no desorption of CH disulfides. We therefore concluded that CH thiolate molecules are able to form disulfides with the C1 thiolate, although CH thiolates do not form CH disulfides. We also investigated the desorption process of the mixed SAM of the CH and C8 thiols (Figure 5b). Based on this investigation, we found the same desorption behavior as observed in the case of the mixed C1-CHT SAM; i.e., only C8 disulfides and C8-CHT disulfides were observed, and there was no desorption of CH disulfides. Our results strongly suggest that the structure of the molecules constituting the SAM is a critical factor in determining the desorption manner. Recently, Ito et al. investigated the desorption process of structural isomers of propanethiols and found that there is an obvious correlation between steric hindrance of the molecules and their desorption behavior,¹⁵ strongly supporting our findings.

Conclusion

In this study, we investigated the thermal desorption processes of the C1 SAM, C8 SAM, and CHT SAM to elucidate the influence

of the terminal groups on the desorption manner. Our results clearly showed that the molecular structures of thiol derivatives critically govern whether or not the dimerization of thiolate molecules takes place during thermal desorption. We expect that suppression of the dimerization of thiolate molecules by introducing bulky groups into the molecule may significantly improve the thermal stability of SAMs of alkanethiols on Au(111).

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- (33) The mixing ratio of solution is not automatically transferred to the surface composition, and it is difficult to estimate the exact composition ration by XPS and TDS. We found that population of C1 and C8 tends to overwhelm that of CHT by simply comparing the area of desorption peaks of C1, C8 disulfides, and CH thiol.