# Mixed Methyl- and Propyl-Thiolate Monolayers on a Au(111) Surface

Jianzhi Gao,[†] Fangsen Li,[†,‡] and Quanmin Guo*[,†]

[†]School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom
[‡]State Key Laboratory of Low-Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, China

ABSTRACT: Mixed methyl- and propyl-thiolate self-assembled monolayers (SAMs) are prepared on a Au(111) surface by exposing the gold substrate to methyl-propyl-disulfide vapor at room temperature. Scanning tunneling microscopy imaging of such SAMs reveals a (3×4) phase consisting of CH_3-S-Au-S-CH_3, CH_3-S-Au-S-$(CH_2)_2CH_3$, and CH_3-$(CH_2)_2$-S-Au-S-$(CH_2)_2CH_3$. Partial desorption of methyl-thiolate occurs when samples are thermally annealed to 373 K, leading to the formation of a striped phase consisting of primarily CH_3-$(CH_2)_2$-S-Au-S-$(CH_2)_2CH_3$.
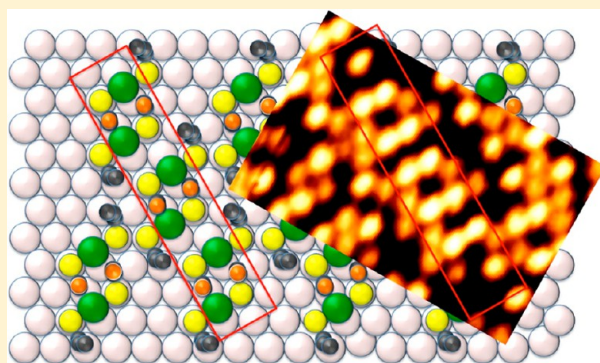
INTRODUCTION

Despite the extensive study of self-assembled monolayers (SAMs) of alkanethiols,[1,2] the nature of the chemical bonding at the thiolate−Au interface is still a matter of debate.[3−6] There is a growing consensus that gold-adatom-dithiolate, RS-Au-SR, is the key structural motif on both Au nanoparticles[7] and the extended gold surface.[8,9] On the other hand, Au-adatom-monothiolate, RS-Au, may also play an important role during the dynamic assembly process.[7,10] Using high-resolution scanning tunneling microscopy (STM) imaging, it has been shown that methyl- and ethyl-thiolate monolayers on Au(111) form a (3×4) phase at saturation coverage of $^1/_3$ monolayer (ML).[11−13] The $(\sqrt{3} \times \sqrt{3})$-R30° structure and its $(3 \times 2\sqrt{3})$-rect./c(4×2) variations, observed for SAMs of longer chain thiols (butyl-thiolate and beyond), do not exist for methyl- and ethyl-thiolate monolayers.[11] Finding the connection between the (3×4) phase and the $(\sqrt{3} \times \sqrt{3})$-R30° phase has thus become a crucial step in developing a satisfactory understanding of alkanethiol SAMs.

Here we report findings of an STM study of mixed methyl- and propyl-thiolate monolayers. Mixed SAMs of the longer chain alkanethiols on Au(111)[14−16] and on Au nanoparticles[17] have been studied in the past. Mixed layers can be prepared by either a single-step co-adsorption process[14] or a two-step adsorption involving ligand exchange.[16,18] We produce the mixed SAMs by exposing the gold substrate to methyl-propyl-disulfide vapor under vacuum.

EXPERIMENTAL SECTION

We conducted experiments in an ultrahigh vacuum (UHV) chamber using an Omicron variable-temperature STM instrument (VT-STM). The gold sample is a (111)-oriented Au film deposited on a highly oriented pyrolitic graphite substrate. The Au film is cleaned *in situ* using cycles of Ar⁺ ion sputtering and thermal annealing. The mixed SAM was prepared by exposing the gold sample to ~10⁻⁵ mbar of methyl-propyl-disulfide (MPDS) vapor at room temperature (RT). MPDS purchased from Sigma-Aldrich was treated with a few freeze−pump−thaw cycles to remove air and other trapped impurities before being introduced into the vacuum chamber. STM imaging was performed using electrochemically etched tungsten tips.

RESULTS AND DISCUSSION

Alkyl disulfide molecules dissociate on gold surfaces at RT,[19] and they subsequently combine with Au atoms to form RS-Au-SR units.[8,9,11] Here we expect to see CH_3S-Au-SCH_3 $(C_1−C_1)$, CH_3S-Au-S$(CH_2)_2CH_3$ $(C_1−C_3)$, and $CH_3(CH_2)_2$S-Au-S-$(CH_2)_2CH_3$ $(C_3−C_3)$ on the Au(111) surface. Figure 1a shows an STM image obtained from the gold sample covered by ~0.2 monolayer (ML) of mixed methyl- and propyl-thiolate. One monolayer is defined as one thiolate (not distinguishing between methyl- and propyl-thiolate) per surface Au atom. The coverage of the "full" layer is $^1/_3$ ML. With this coverage, the mixed SAM is disordered at RT as observed with the STM, and hence, the image in Figure 1a was acquired at 115 K. Here we see the typical striped phase frequently observed for many alkylthiolate monolayers at less than the saturation coverage. Bright spots along each stripe parallel to the ⟨112⟩ directions are separated by 0.5 nm. The interstripe distance is not 100% regular but has a typical value of 1.3 nm that is ~4.5a, where a is the atomic spacing on Au(111). The domains consisting of parallel stripes have similar characteristics with those found for ethyl-thiolate[20−22] and propyl-thiolate monolayers.[9,23] A closer examination reveals that there are three types of striped rows. One type, seen as two parallel rows of spots as highlighted by the blue colored arrows in panels a and b of Figure 1, is assigned to the $C_3−C_3$ rows. This double-row feature is also
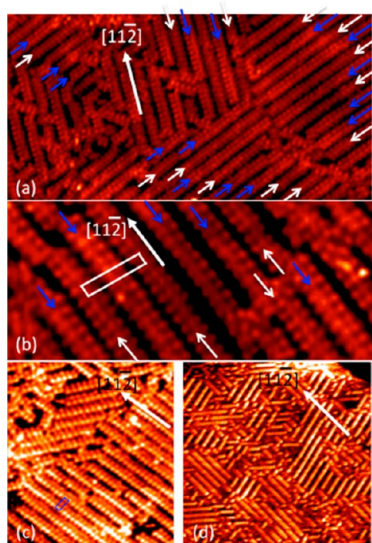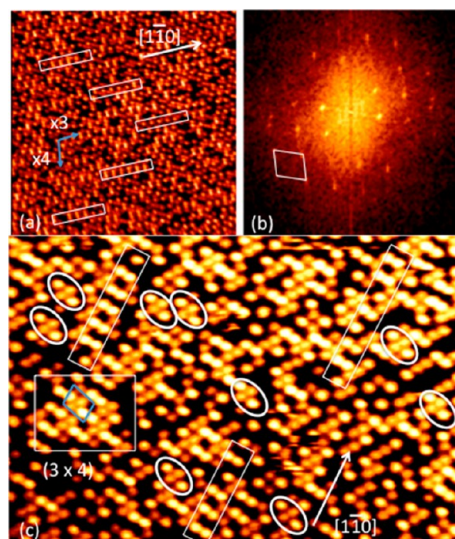
Figure 1. (a) STM image (30 nm × 16 nm) obtained using a −0.25 V sample bias and a 0.4 nA tunneling current at 115 K from Au(111) with 0.2 ML of a mixed methyl- and propyl-thiolate monolayer. (b) Magnified view showing the alternating C_1–C_1 and C_3–C_3 rows. (c) STM image (15 nm × 17 nm) obtained using a −1.0 V sample bias and a 0.1 nA tunneling current, showing C_1–C_3 rows along the $[11\bar{2}]$ direction. (d) STM image (33 nm × 33 nm) obtained using a −1.4 V sample bias and a 0.1 nA tunneling current at 200 K. Disordering starts at the boundaries.

Figure 2. (a) STM image (25 nm × 25 nm) obtained using a −1.5 V sample bias and a 0.2 nA tunneling current from Au(111) with a saturation layer of mixed methyl- and propyl-thiolate monolayers. Rectangles are drawn to highlight ordered array of spots. (b) FFT of the image in panel a. A 3 × 4 unit cell is illustrated. (c) STM image (17 nm × 11 nm) obtained using a −1.5 V sample bias and a 0.2 nA tunneling current after the sample was thermally annealed at 323 K for 30 min.

present in the striped phase of ethyl-thiolate monolayers.[20−22] The second type, consisting of three rows of spots as denoted by the white arrows, is assigned to the C_1–C_1 rows. Here, CH_3 and the Au adatom appear as protrusions.[9,11] In Figure 1b, a rectangular unit cell is illustrated. The unit cell is $9a$ long and $\sqrt{3}a$ wide. At 115 K, there is some anisotropic thermal drift, making the numerical measurement of distances less reliable. The $9a$ distance should be regarded as a guideline value rather than an accurate determination of the unit cell dimension. Figure 1c shows the third type of striped rows. In this case, each stripe consists of two rows of spots with different heights. We assign this type as the asymmetric C_1–C_3 rows with the C_3 chain appearing taller than C_1. An indicative rectangular unit cell, $4.5a \times \sqrt{3}a$, is illustrated in the figure. On the basis of the analysis described above, we draw the conclusion that the striped phase of the mixed thiolate monolayer consists of domains of alternating C_1–C_1 and C_3–C_3 rows and domains of C_1–C_3 rows. Increasing the temperature causes disordering initially at the domain boundaries (Figure 1d). A complete loss of ordering occurs at 250 K. For both ethyl- and propyl-thiolate monolayers, stable striped phases are observed at RT.[20,23] Therefore, the lower stability of the striped C_1/C_3 mixture is caused by the presence of the methyl-thiolate.

In contrast to the striped phase at 0.2 ML, a stable structure is observed at RT when the surface is covered by $^1/_3$ ML of the mixed thiolate. Figure 2a shows an STM image of the mixed SAM formed on Au(111) following an exposure to MPDS at a pressure of 2×10^{-5} mbar for 1 h. A first glance of the image gives the impression that long-range order is lacking, but short-range order is clearly identified as shown by the ordered rows of spots inside the rectangles. On the basis of previous experience with methyl- and ethyl-thiolate monolayers,[11] we can assign the bright spots in the image to the methyl groups of the alkane chains. A fast Fourier transform (FFT) of Figure 2a

is shown Figure 2b, which exhibits a 3 × 4 lattice. The directions of the unit vectors along the ×3 and ×4 directions are shown in Figure 2a. We do not show a unit cell because it would be too small in the figure.

To improve the long-range order of the SAM, the sample was then thermally annealed at 323 K for 30 min. Figure 2c shows an image obtained after the annealing process. The ordered arrays of paired spots highlighted by the rectangles suggest that the ordering has been improved. Near the lower left corner of the image, there is a small patch showing a perfectly ordered (3 × 4) phase. Any signs of the (3 × 4) phase on the surface is direct evidence that the global coverage is very close to $^1/_3$ ML.[11] Figure 2c, however, gives the impression that the coverage is rather low. This is because at RT only C_3 appears as protrusions in the image. The dark areas in the image are not empty space. Instead, they are places where C_1 is hidden. By simply counting the number of protrusions in Figure 2c, we find that the observed protrusions (C_3) have a density of 2.6 nm^{-2}. This amounts to 56% of $^1/_3$ ML. Thus, the monolayer is slightly enriched in C_3 with a C_1:C_3 ratio of 0.44:0.56.

Following the same scheme used for methyl- and ethyl-thiolate monolayers,[7,11] we present a ball model for a propyl-thiolate monolayer in Figure 3. The (3 × 4) phase consists of zigzag rows of C_3–C_3 chains. Each C_3–C_3 chain has two propyl chains: an α chain and a β chain. The two chains have the same composition and structure, but different tilt angles toward the surface. The β chain, being sandwiched between the S atom and the Au adatom of the adjacent C_3–C_3 chain, stands more perpendicular to the surface than the α chain. Thus, the α and the β chains appear with different heights giving rise to the observed contrast in the STM image. In Figure 3, a red rectangle is used to mark an array of paired β chains. There is a good agreement between the model and the STM image of Figure 2c.
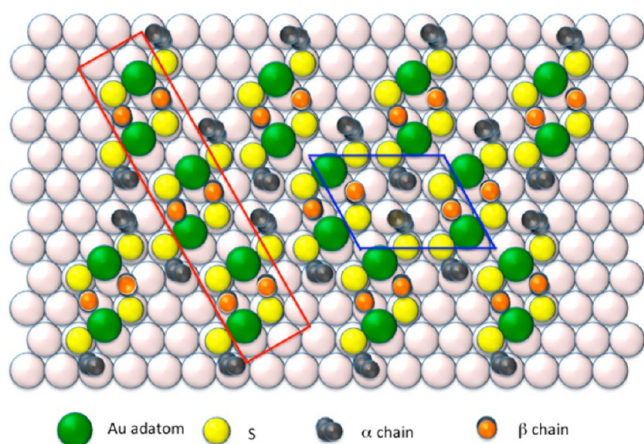
Figure 3. Ball model of the (3×4) phase of a propyl-thiolate monolayer consisting of Au-adatom-dithiolate units. The α chain tilts more toward the surface than the β chain. This makes the β chain taller as observed in STM images.

In Figure 2c, the monolayer consists of C_1–C_1, C_1–C_3, and C_3–C_3 chains. However, only C_3 chains appear as protrusions in the image. Knowing that R_1S-Au-SR_2 is the basic structural motif, we can locate the hidden C_1 chains in Figure 2c by performing a simple "pairing up" procedure. The only condition that we apply is that a C_3 observed in the image must be paired with another C_3 or C_1 following the rules given by Figure 3. This pairing procedure allows us to locate C_1 in the dark areas as indicated in Figure 4a. In Figure 4a, we overlay spheres onto the STM image: yellow spheres represent the β chains (C_1 or C_3) and blue spheres the α chains (C_1 or C_3). The array of blue and yellow spheres gives a long-range ordered (3×4) phase. In Figure 4b, red spheres are used to highlight the hidden C_1 discovered using the pairing procedure, regardless of whether they occupy the α or β position. The C_1–C_1:C_3–C_3:C_1–C_3 ratio within the area analyzed is 0.13:0.78:1. In the image, there are a number of dark areas that are much larger than the size of the unit cell. These areas are probably covered completely by C_1–C_1 chains. In our analysis, we ignored these dark areas rather than attempting to fill them with C_1–C_1 chains. If we assume that these dark areas are covered by C_1–C_1 chains, it would bring the C_1–C_1:C_3–C_3:C_1–C_3 ratio to 0.19:0.35:0.45. Statistically, a 0.25:0.25:0.5 ratio is expected. The low content of C_1–C_1 chains may arise from a possible substitution of C_1 by C_3 during exposure to DMDS.

A rather common feature in Figure 2c is the grouping of two α C_3 chains with two β C_3 chains into a diamond-shaped structure. Several such structures are highlighted with white ovals in Figure 2c. Figure 5 presents a ball model explaining the formation of such local structures. According to the scheme in Figure 5, when four C_1–C_3 units join to form the (3×4) phase, there is the tendency for the C_3 chains to move close to each other, likely as a result of the van der Waals interaction. This effect is visually more striking when these four C_1–C_3 units are surrounded by C_1–C_1 units as seen in Figure 2c.

A previous study has already confirmed that the only stable structure for a methyl- or ethyl-thiolate monolayer on Au(111) at saturation coverage is (3×4).[11] Here we demonstrate that for the mixed SAM of methyl- and propyl-thiolate, the same type of (3×4) arrangement is achieved. Since the submission of this work, we have examined a propyl-thiolate (PT)

(a)

(b)
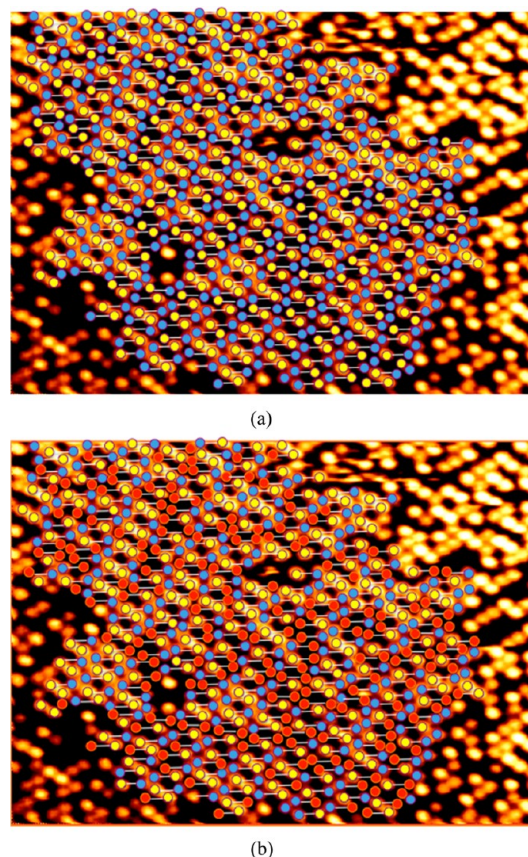
Figure 4. Application of the pairing procedure to the image shown in Figure 2c. (a) The yellow and blue spheres represent all the thiolate species identified by the pairing procedure. (b) Red spheres highlight the hidden C_1. Yellow spheres and blue spheres represent C_3 at the β and α positions, respectively.
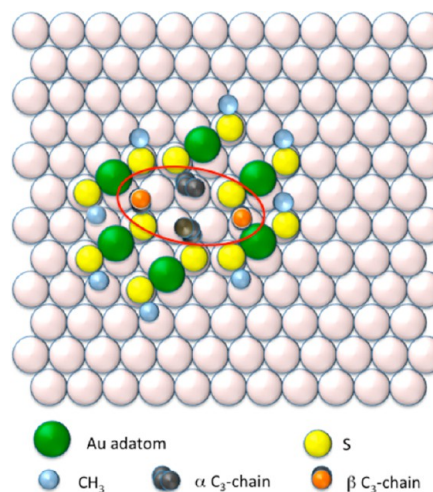

Figure 5. Ball model showing the preferential grouping of the C_3 chains. The two α chains and the two β chains inside the red-colored oval form the diamond-shaped structure in Figure 2c.

monolayer on its own and found that a PT monolayer also forms the same (3×4) structure. Now we have a clear dividing line between propyl-thiolate and butyl-thiolate (BT) monolayers. On one side of this line, we have the (3×4) structure; on the other side, we have the $(3 \times 2\sqrt{3})/c(4 \times 2)$ structure. This allows us to reach a conclusion that moving from PT to

BT, the van der Waals interaction between the alkane chains has grown to a critical strength to initiate a gross structural change at the interface.

When the mixed SAM is further annealed to 373 K, partial desorption takes place. The remaining thiolate on the surface forms a long-range ordered striped phase. Figure 6 shows such
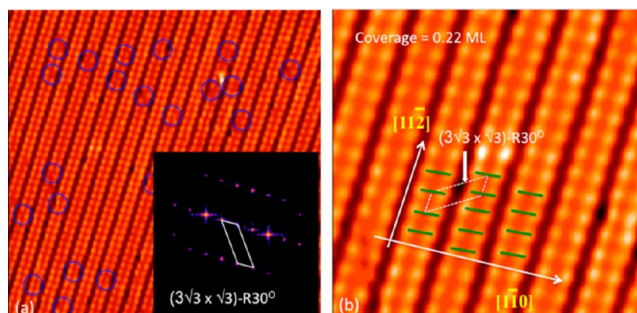
Figure 6. (a) STM image (25 nm × 25 nm) obtained using a −1.0 V sample bias and a 0.05 nA tunneling current, showing the striped phase of propyl-thiolate. Blue circles highlight possible residual C_1–C_3 units. The inset is an FFT of the image showing the high quality of ordering and the $(3\sqrt{3} \times \sqrt{3})$-R30° unit cell. (b) Magnified view of the $(3\sqrt{3} \times \sqrt{3})$-R30° phase. Green colored bars indicate C_3–C_3 units.

a striped phase after the sample had been annealed at 373 K for 30 min. The striped phase shown in Figure 6 has a $(3\sqrt{3} \times \sqrt{3})$-R30° unit cell. In contrast to the striped phase of the mixed SAM shown in Figure 1, this striped phase is stable at RT. This striped phase consists of C_3–C_3 rows as illustrated in Figure 7. The majority of C_1 has been desorbed. In Figure 6a,
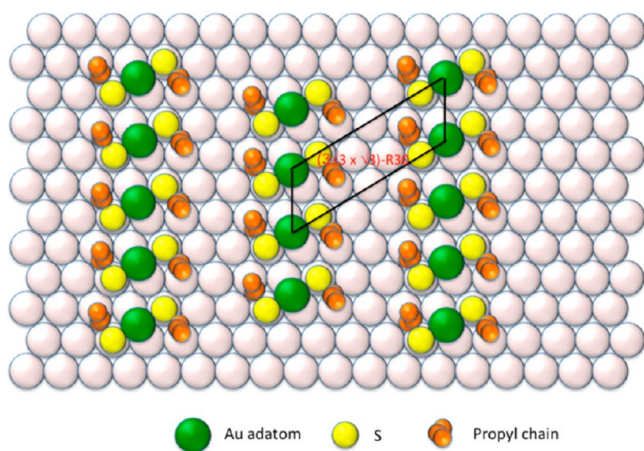
Figure 7. Ball model of the $(3\sqrt{3} \times \sqrt{3})$-R30° striped phase. Adjacent C_3–C_3 rows are separated by 4.5a ($a = 0.288$ nm) along the $[1\bar{1}0]$ direction and offset by $\sqrt{3}/2a$ along the $[11\bar{2}]$ direction.

each C_3–C_3 row consists of two rows of spots with equal intensity. There are a small number of faint spots indicating the existence of residual C_1–C_3 chains within the layer.

CONCLUSIONS

A mixed methyl- and propyl-thiolate monolayer forms a (3 × 4) phase at $^1/_3$ ML coverage at RT. The (3 × 4) phase comprises almost a random mixture of C_1–C_1, C_1–C_3, and C_3–C_3 units. The limited level of phase separation into pure C_1–C_1 and C_3–C_3 domains occurs after the sample has been

thermally annealed to 323 K, but the domain size is only a few unit cells in size. Thermal treatment at 373 K causes nearly complete desorption of C_1 from the surface, with the remaining C_3 forming a stable striped $(3\sqrt{3} \times \sqrt{3})$-R30° phase.

AUTHOR INFORMATION

Corresponding Author
*E-mail: q.guo@bham.ac.uk. Fax: +44 1214147327.
Notes
The authors declare no competing financial interest.

REFERENCES

(1) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chem. Rev.* **2005**, *105*, 1103.
(2) Kind, M.; Wöll, Ch. Organic surfaces exposed by self-assembled organothiol monolayers: Preparation, characterization, and application. *Prog. Surf. Sci.* **2009**, *84*, 230.
(3) Hakkinen, H. The gold-sulfur interface at the nanoscale. *Nat. Chem.* **2012**, *4*, 443.
(4) Maksymovych, P.; Voznyy, O.; Dougherty, D. B.; Sorescu, D. C.; Yates, J. T., Jr. Gold adatom as a key structural component in self-assembled monolayers of organosulfur molecules on Au(111). *Prog. Surf. Sci.* **2010**, *85*, 206.
(5) Ferrighi, L.; Pan, Y.-X.; Gronbeck, H.; Hammer, B. Study of alkylthiolate self-assembled monolayers on Au(111) using a semilocal meta-GGA density functional. *J. Phys. Chem. C* **2012**, *116*, 7374.
(6) Carro, P.; Pensa, E.; Vericat, C.; Salvarezza, R. C. Hydrocarbon chain length induces surfaces structure transitions in alkanethiolate-gold adatom self-assembled monolayers on Au(111). *J. Phys. Chem. C* **2013**, *117*, 2160.
(7) Maksymovych, P.; Sorescu, D. C.; Voznyy, O.; Yates, J. T. Hybridization of phenylthiolate- and methylthiolate-adatom species at low coverage on the Au(111) surface. *J. Am. Chem. Soc.* **2013**, *135*, 4922.
(8) Maksymovych, P.; Sorescu, D. C.; Yates, J. T., Jr. Gold-adatom-mediated bonding in self-assembled short-chain alkanethiolate species on the Au(111) surface. *Phys. Rev. Lett.* **2006**, *97*, 146103.
(9) Voznyy, O.; Dubowski, J. J.; Yates, J. T., Jr.; Maksymovych, P. The role of gold adatoms and stereochemistry in self-assembly of methylthiolate on Au(111). *J. Am. Chem. Soc.* **2009**, *131*, 12989.
(10) Yu, M.; Bovet, N.; Satterley, C. J.; Bengio, S.; Lovelock, K. R. J.; Milligan, P. K.; Jones, R. G.; Woodruff, D. P.; Dhanak, V. True nature of an archetypal self-assembly system: Mobile Au-thiolate species on Au(111). *Phys. Rev. Lett.* **2006**, *97*, 166102.
(11) Tang, L.; Li, F. S.; Zhou, W.-C.; Guo, Q. The structure of methylthiolate and ethylthiolate monolayers on Au(111): Absence of the $(\sqrt{3} \times \sqrt{3})$R30° phase. *Surf. Sci.* **2012**, *606*, L31.
(12) Kondoh, H.; Nozoye, H. Low-temperature ordered phase of methylthiolate monolayers on Au(111). *J. Phys. Chem. B* **1999**, *103*, 2585.
(13) Kawasaki, M.; Nagayama, H. Observation of highly ordered 3 × 4 phase of ethanethiol self-assembled monolayer on Au(111). *Chem. Lett.* **2001**, *30*, 942.
(14) Li, L.; Chen, S.; Jiang, S. Molecular-scale mixed alkanethiol monolayers of different terminal groups on Au(111) by low-current scanning tunneling microscopy. *Langmuir* **2003**, *19*, 3266.
(15) Heister, K.; Allara, D. L.; Bahnck, K.; Frey, S.; Zharnikov, M.; Grunze, M. Deviations from 1:1 compositions in self-assembled monolayers formed form adsorption of asymmetric diakyl disulfides on gold. *Langmuir* **1999**, *15*, 5440.
(16) Lussem, B.; Muller-Meskamp, L.; Karthauser, S.; Waser, R.; Homberger, M.; Simon, U. STM study of mixed alkanethio/

biphenylthiol self-assembled monolayers on Au(111). *Langmuir* **2006**, *22*, 3021.

(17) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. Dynamics of place-exchange reactions on monolayer-protected gold cluster molecules. *Langmuir* **1999**, *15*, 3782.

(18) Heinecke, C.; Ni, T. W.; Malola, S.; Makinen, V.; Wong, O. A.; Hakkinen, H.; Ackerson, C. J. Structural and theoretical basis for ligand exchange on thiolate monolayer protected gold nanoclusters. *J. Am. Chem. Soc.* **2012**, *134*, 13316.

(19) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. Fundamental-studies of the chemisorption of organosulfur compounds on Au(111): Implications for molecular self-assembly on gold surfaces. *J. Am. Chem. Soc.* **1987**, *109*, 733.

(20) Li, F.-S.; Tang, L.; Voznyy, O.; Gao, J.-Z.; Guo, Q. The striped phases of ethylthiolate monolayers on the Au(111) surface: A scanning tunneling microscopy study. *J. Chem. Phys.* **2013**, *138*, 94707.

(21) Li, F.-S.; Tang, L.; Gao, J.-Z.; Zhou, W.-C.; Guo, Q. Adsorption and electron-induced dissociation of ethanethiol on Au(111). *Langmuir* **2012**, *28*, 11115.

(22) Clair, S.; Kim, Y.; Kawai, M. Coverage-dependent formation of chiral ethylthiolate-Au complexes on Au(111). *Langmuir* **2011**, *27*, 627.

(23) Wang, Y.; Chi, Q.; Hush, N. S.; Reimers, J. R.; Zhang, J.-D.; Ulstrup, J. Gold mining by alkanethiol radicals: Vacancies and pits in the self-assembled monolayers of 1-propanethiol and 1-butanethiol on Au(111). *J. Phys. Chem. C* **2011**, *115*, 10630.