

Controlling the Stereochemistry and Regularity of Butanethiol Self-Assembled Monolayers on Au(111)

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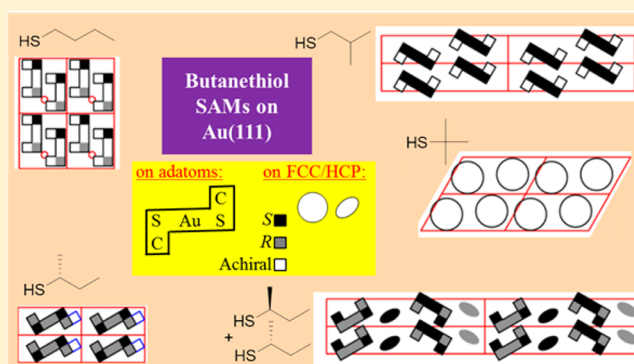
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Supporting Information

ABSTRACT: The rich stereochemistry of the self-assembled monolayers (SAMs) of four butanethiols on Au(111) is described, the SAMs containing up to 12 individual C, S, or Au chiral centers per surface unit cell. This is facilitated by synthesis of enantiomerically pure 2-butanethiol (the smallest unsubstituted chiral alkanethiol), followed by in situ scanning tunneling microscopy (STM) imaging combined with density functional theory molecular dynamics STM image simulations. Even though butanethiol SAMs manifest strong headgroup interactions, steric interactions are shown to dominate SAM structure and chirality. Indeed, steric interactions are shown to dictate the nature of the headgroup itself, whether it takes on the adatom-bound motif $RS^*Au(0)S^*R$ or involves direct binding of RS^* to face-centered-cubic or hexagonal-close-packed sites. Binding as RS^* produces large, organizationally chiral domains even when R is achiral, while adatom binding leads to rectangular plane groups that suppress long-range expression of chirality. Binding as RS^* also inhibits the pitting intrinsically associated with adatom binding, desirably producing more regularly structured SAMs.



1. INTRODUCTION

The formation of self-assembled monolayers (SAMs) of small molecules offers unique insight into the interactions among headgroup forces, substrate-relaxation forces, and intermolecular steric interactions in the manifestation of surface chirality. Surface chirality can manifest if the adsorbate molecules are themselves chiral, if the atomic structures formed at the interface are chiral, or if the macroscopic arrangement of adsorbate molecules is chiral,^{1–6} and indeed all effects may operate concurrently, leading to complex surface stereochemistry. Chiral surfaces, no matter by what means they are formed, are of general interest for chiral resolution^{7,8} and catalysis.^{9–11} Control of chirality could also be critical to any single-molecule device assembled on a surface. Often large molecules are preferred for consideration, as the steric repulsions and intermolecular attractions stemming from their geometric structure typically serve to control the monolayer plane group. This is what leads to the observed propensity of plane groups embodying two-fold rotations in packing motifs, groups that do not intrinsically destroy global chirality.^{2,5}

Hence most SAMs pack into chiral structures, in contrast to most crystals for which the same steric packing forces lead to a preference for centrosymmetric arrangements that are intrinsically achiral. However, when the molecules become small enough so that steric interactions no longer obviously control the structure, the headgroup interaction could dominate to control SAM chirality.

Here we describe the chirality properties of the SAMs formed by the butanethiols (Chart 1), a family of adsorbate molecules that includes the smallest unsubstituted chiral alkanethiol, 2-butanethiol. We analyze established structural properties for SAMs of the linear isomer 1-butanethiol (L),^{12–14} the branched achiral isomer 2-methyl-1-propanethiol (B),^{15,16} the tertiary isomer 2-methyl-2-propanethiol T,^{15,17} and a racemic mixture (R)¹⁸ of the enantiomer forms of 2-butanethiol ((R)-C and (S)-C). In addition, we present the in situ synthesis of the pure R- and S-enantiomeric forms of 2-

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3. RESULTS

3.1. STM Images of the Enantiomerically Pure 2-Butanethiols and SAM Observation. The STM images of both SAMs indicate assembly into the $(4\times\sqrt{3})-2$ lattice, see Figure 1 and SI, section S4. The presence of two molecules per

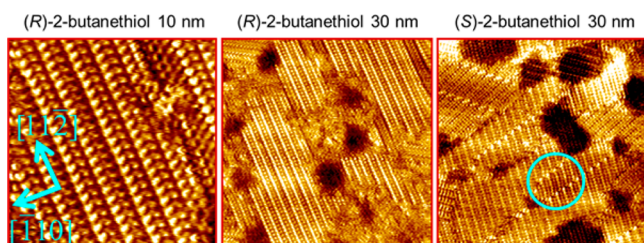


Figure 1. STM images of SAMs of chemisorbed (*R*)-2-butanethiol (tunneling current $I_t = 0.04$ nA, bias voltage $V_{\text{bias}} = 0.10$ V) and (*S*)-2-butanethiol ($I_t = 0.08$ nA and $V_{\text{bias}} = 0.40$ V). The blue circle highlights two domain boundaries.

unit cell was confirmed by reductive desorption experiments (see SI, section S6) depicting sharp desorption peaks at -0.816 ± 0.01 and -0.818 ± 0.01 V vs saturated calomel electrode, the areas of which indicate adsorbate coverages of $(6.2 \pm 0.4) \times 10^{-10}$ and $(6.4 \pm 0.4) \times 10^{-10}$ mol cm^{-2} for (*S*)-2-butanethiol and (*R*)-2-butanethiol, respectively, close to the anticipated value for two molecules per cell of 5.8×10^{-10} mol cm^{-2} . The adsorbate coverage is therefore 25%. Repetition of this procedure using a 50:50 mixture of the *S*-*sec*-butyl ethanthioate enantiomers yields a higher-density SAM indistinguishable from that determined previously¹⁸ using commercial racemic 2-butanethiol adsorbate.

Images of the *R* stereoisomer were obtained at length scales down to $10 \text{ nm} \times 10 \text{ nm}$, whereas only $30 \text{ nm} \times 30 \text{ nm}$ images were stable for *S*. These images clearly show two spots per surface cell with one brighter than the other, plus a darker region. Although the SAMs show global point chirality, they assemble into rectangular unit cells with nearly collinear internal structural features, minimizing visualization of long-range manifestations of chirality. Domain boundaries between possibly mirror-image forms can be found, however, as highlighted in the figure.

The larger-area scans in Figure 1 show the presence of disordered regions, which in places cover up to $\sim 15\%$ of the surface, and also pitted regions of the surface. Section S5 in the SI analyzes some larger-area scans, identifying the pits as covering ca. 10% of the surface. Pits are formed when adatoms are mined, and as large terraces are used to prevent mining from step edges and also as in these experiments the gold $(22\times\sqrt{3})$ reconstruction is lifted *before* SAM formation, all adatoms must come from pits. Because the $(4\times\sqrt{3})-2$ lattice contains 10 gold atoms per layer, a 10% pit coverage therefore implies the presence of one additional gold atom per cell. SAMs may also contain local vacancies in the top gold layer,^{22,62-64} so the observed pit coverage could be accounted for by atomic structures containing per cell either one adatom and no local vacancy (1A0V) or else two adatoms and one vacancy (2A1V).

3.2. DFT Simulation of STM Images of Enantiomerically Pure 2-Butanethiol SAMs. With 2 adsorbate molecules per surface cell, the observed SAMs possess a significant configuration space of possible atomic structures. To process this, two classes of geometric variables controlling the structure were identified: (1) chemical descriptors specifying the locations of the gold and sulfur atoms, and (2) three torsional

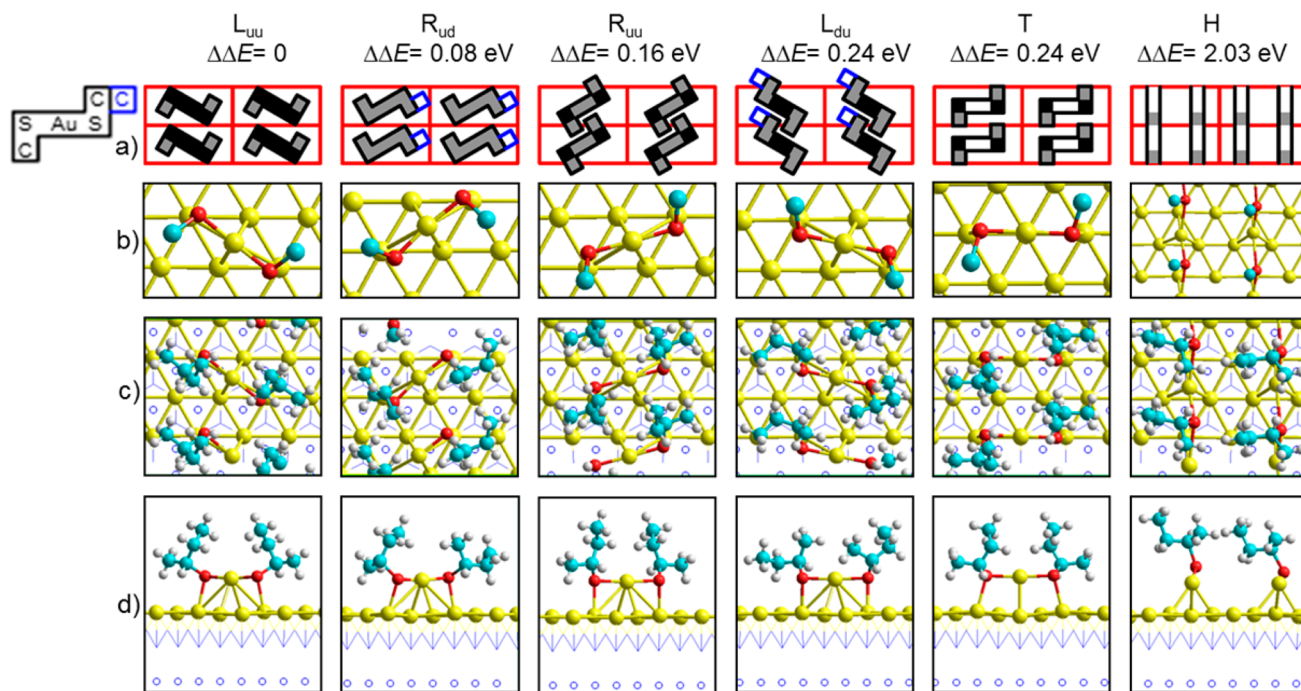


Figure 2. Four copies of DFT optimized structures and energies depicting the observed SAMs of (*R*)-2-butanethiol on Au(111). Rows (b) and (c) show top views of the SAM, restricted to just the surface gold layer and a single C–S–Au–S–C unit in b); sulfur (red), carbon (cyan), hydrogen (white), gold top layer and adatoms (yellow), gold subsurface layer (blue bond to top layer), gold third layer (blue open circles), gold fourth layer not shown. Row (d) shows the side view corresponding to row (c). Row (a) shows caricatures of row b), highlighting the stereochemistry at the C–S–Au–S–C centers: *R* (gray), *S* (black), or achiral (white), while blue squares indicate flat lying ethyl groups.

angles (Au–S, S–C, and C–C) per adsorbate specifying conformational details. We considered all known possible sulfur arrangements explicitly, and for each of these scanned the torsional-angle spaces using a product grid search involving the examination of ca. 10^5 possible structures. These were pre-screened by selecting only 100–200 structures with nonbonded C–C distances in excess of 3.2 Å for which DFT optimizations were then run. All calculations were constrained to the observed $(4\times\sqrt{3})-2$ substrate lattice, but the numbers of gold atoms and surface vacancies were varied.

Four stable chemical structures depicting the gold and sulfur headgroup atoms were identified, all containing gold adatoms bound to two sulfur atoms and the surface. Structures with adsorbate molecules bound directly to the Au(111) surface relaxed to spontaneously lift an adatom off the surface to make a local vacancy, while structures in which a gold adatom was bound to just a single sulfur atom led to polymerization. The four stable chemical structures are shown in Figure 2 and are denoted H (horizontal), L (left), R (right), and T (top) after the location of the gold adatoms with respect to the substrate (see SI, Figure S7). Stable conformers were always found for the two gauche arrangements G_+ and G_- as well as for the higher-energy anti conformer A of the C–C torsion of each adsorbate molecule. For the L and R species, all other torsional variables were found to be tightly coupled, leading to only two stable molecular configurations. These may be effectively characterized based on the involved C–S torsional angles: in one case both adsorbate molecules have their ethyl groups erecting vertically from the surface, uu (structures named L_{uu} and R_{uu}), and in the other case one erects while one is oriented in the surface plane, ud (named $L_{ud} \equiv L_{du}$ and $R_{ud} \equiv R_{du}$). Hence a total of six stable structural types were found. The calculated energies for all nine possible C–C conformers of these are given in SI, section S7a, while the lowest-energy structure of each type is shown in Figure 2. Summarizing the results, a set of empirical rules depicting low-energy structures is developed in SI, section S7b.

Shown on the top row of Figure 2 are sketches depicting each structure's geometry and chirality. Every atom in the C–S–Au–S–C central unit can take on enantiomeric forms, indicated in the figure by shading (S is black, R is gray, achiral is white). Figure 2 applies only to (R)-2-butanethiol SAMs, and so all end units in this figure are shaded gray; analogous structures for (S)-2-butanethiol SAMs may be obtained simply by reflection, interchanging all stereocenters (see SI, section S7a). For the gold adatom, the L site is S, while the R site is R and the H and T sites are achiral. The sulfur atoms may take on either enantiomeric form, however, controlling the overall molecular shape;⁶ only RR or SS sulfur configurations appear in Figure 2, indicating that all adatom motifs take on a syn (often called *cis*)^{6,63} structure. The SR and RS sulfur configurations are known for B and R, however,^{15,16,18,63} producing anti (often called *trans*)^{6,63} structures.

The lowest-energy structure is found to be L_{uu} , but R_{ud} is only $\Delta E = 0.08$ eV higher; this difference is below the accuracy of the method and of the order of likely entropy corrections to the Gibbs free energy. At $\Delta E = 0.16$ eV, R_{uu} may also be feasible, but the L_{du} and T structures are unlikely, having $\Delta E = 0.24$ eV, while H is of very high energy at $\Delta E = 2.03$ eV.

The T structure has the gold adatoms sitting vertically above a gold surface atom instead of being at a bridge site. Indeed, all other structures utilize one of the three (L, R, H) bridge sites, see SI, Figure S7. For achiral adsorbates the L and R sites are

equivalent, but chiral adsorbates discriminate between them. The high-energy H structure assembles the adsorbate molecules into two parallel infinite chains per surface cell of the form –S–Au–S–Au–S. As such, this structure includes two adatoms per surface cell and so to be consistent with the observed pit coverage there must also be one local vacancy per cell (2A1V). However, we find for all six structural types shown in Figure 2, formation of pits from local gold surface vacancies is considerably exothermic by of order 2 eV, in contrast to the –0.20 to 0.04 eV energy differences found for the other butanethiols.⁶³ Structure T is thus predicted to have two adatoms and no vacancies (2A0V) and hence be inconsistent with the experimental data. The other five structures all have one adatom and no vacancy (1A0V) and are therefore consistent with it.

To investigate effects of thermal motion manifest on a short time scale,^{14,16,21,22,65,66} DFT MD simulations at 300 K were performed for each of the nine conformations of the L_{uu} structure obtained by rotating about the C–C torsion angles. The resulting torsional-angle probability distributions (see SI, section S7c) reveals that only three of the forms are stable on the 10 ps time scale. The nudged elastic band method was then applied to find transition-state energies linking these three structures, evaluated to be 0.3 eV for a concerted transition state. While transformations between structures will proceed sequentially, this small concerted-reaction barrier clearly indicates that the interconversion of all structures will happen on the 1 m STM time scale. The STM image of L_{uu} is therefore predicted to be symmetric, inconsistent with the bright-spot dull-spot observed pattern.

Structure L_{ud} is intrinsically asymmetric, however, owing to one adsorbate molecule having an ethyl group oriented vertically while the other is horizontal, see Figure 1. Molecular dynamics simulations on the 10 ps time scale induce only local motions in this densely packed structure and the calculated STM image varies little and is in good agreement with the observed image, as shown in Figure 3. It appears that the observed structure is indeed L_{ud} . In previous studies of butanethiol SAMs, the calculated structure of second-lowest energy was sometimes also found to only be consistent with the observed STM image,⁶³ but the largest error previously found was 0.03 eV compared to 0.08 eV here.

However, the alternate domain of structure R_{du} would have the same energy as R_{ud} and hence there must be no equilibration on the STM time scale. Indeed, the appearance of two symmetrically related domains can be seen in the zoomed-out images in Figure 1 which show fault lines in the images across which the bright spots and dull spots interchange. Equilibration of asymmetric variants of the L_{uu} structure was predicted to be very rapid as it involved only uncoupled local motions on each individual adsorbate molecule. However, tilting the ethyl groups downward introduces a strong interaction between adsorbate molecules on adjacent adatoms, with for example global structures of the form R_{dd} not allowed. Therefore, the first step in any interchange process must be the conversion of R_{ud} to R_{uu} , which from SI Table S1 is endothermic by 0.1–0.2 eV. As the calculations appear to underestimate the energy of L_{uu} compared to R_{ud} by at least 0.08 eV, this energy cost may indeed be significantly higher. Such an interchange allows a neighboring adatom complex to change from R_{ud} to R_{du} (see SI, section S7d) at a significant energy cost, but the effect is local and any subsequent change requires still more energy. Chemical structure variations in the

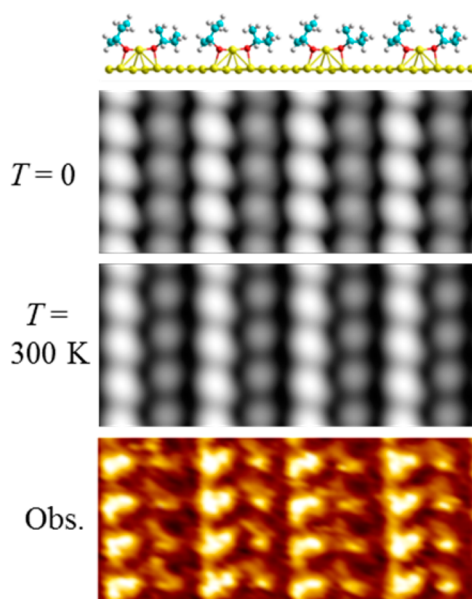


Figure 3. SAM of (R)-2-butanethiol on Au(111) showing a 4×4 grid of $(4 \times \sqrt{3})-2$ surface cells: (top) simulated STM image at 0 K and associated atomic structure R_{ud} , (middle) simulated STM image for R_{ud} following 10 ps MD at 300 K, and (bottom) observed image; sulfur (red), carbon (cyan), hydrogen (white), gold (yellow).

center of domains are thus prevented. Variations could be initiated at domain boundaries, but their propagation would still involve an energy cost. A variety of trial calculations reported in SI section S7d qualitatively support the hypothesis that the R_{ud} structure is locked.

3.3. DFT Simulation of STM Images of the Low-Density Phase of Racemic 2-Butanethiol SAMs. SAMs produced from racemic mixtures of the two 2-butanethiols have previously been studied,¹⁸ revealing a major phase R_{30} consisting of a $(10 \times \sqrt{3})-6$ domain (30% coverage) with nearly pg symmetry. The chirality and structure of its six adsorbate molecules per cell were assigned as “(SR)R(RS)S”, meaning, in order: “(SR)”, one S and one R adsorbate on an adatom; “R”, one R adsorbate molecule on a FCC Au(111) site; “(RS)”, one R and one S adsorbate on an adatom; and finally “S”, one S adsorbate on a HCP lattice site. In this notation, the SAMs of the previously considered chirally resolved molecules are described as being either (RR) or (SS). However, an unassigned minor domain R_{25} was also observed for SAMs made from the racemate of the form $(8 \times \sqrt{3})-4$ (25% coverage) with pg symmetry. Application of the methods developed herein for the chirally resolved SAMs to this structure yield two possibilities of form (SR)(RS) and (RS)(RS). Of these, (SR)(RS) is lower in energy by 0.03 eV and has the observed pg symmetry whereas (RS)(RS) only has $p1$ symmetry and leads to a calculated STM image quite different from that observed. The calculated (SR)(RS) structure is given in Figure 4 where its calculated STM image at 0 K is shown to be in good agreement with the observed¹⁸ image. An alternative possibility for a SAM at 25% coverage is that it forms into separate $(4 \times \sqrt{3})-2$ $p1$ domains of individual characters (RR) and (SS), involving spontaneous chiral resolution of the racemate. We calculate the energies of such domains to be 0.03 eV higher than that of the (SR)(RS) domain.

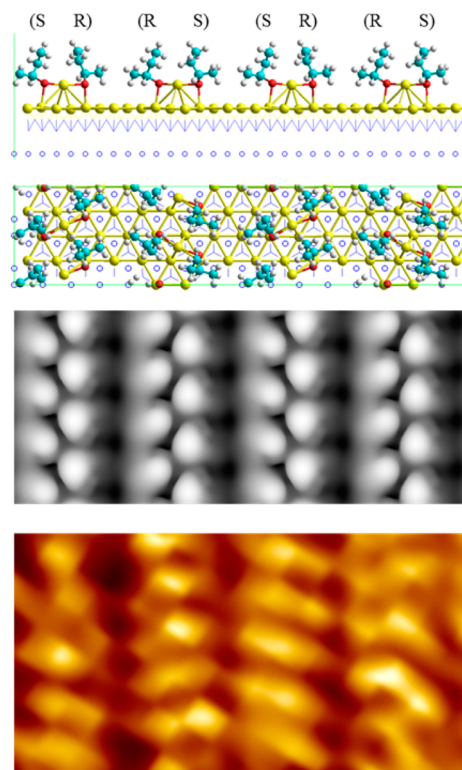


Figure 4. SAMs from a racemic mixture of the 2-butanethiols on Au(111) showing 4×4 surface cells: (top) simulated STM image at 0 K and associated atomic structure of (SR)(RS) chirality, and (bottom) observed image for the $(8 \times \sqrt{3})-4$ phase; sulfur (red), carbon (cyan), hydrogen (white), gold top layer and adatoms (yellow), gold subsurface layer (blue bond to top layer), gold third layer (blue open circles), gold fourth layer not shown.

4. DISCUSSION: CHIRALITY OF THE BUTANETHIOL SAMs ON Au(111)

Table 1 indicates that the butanethiol isomers all show different surface-cell lattices, as dictated by their different steric interactions, very different headgroup arrangements, and very different chirality properties; sketches of these properties are shown in Figure 5. The headgroup properties are indeed widely varied, embracing both syn and anti adatom motifs as well as sulfur groups bound directly onto both Au(111) FCC and HCP sites (indicated by circles and ellipses in Figure 4). Also, the headgroup interaction sometimes involves local vacancy formation. In general, the energetics controlling the headgroup pattern are delicately balanced,⁶³ allowing steric interactions to modulate substrate relaxation effects to in effect control the whole assembly process.

Isomer T with its bulky tertiary carbon forms into the spacious $(2\sqrt{7} \times \sqrt{7})-2$ lattice with a surface coverage of just 1/7. The plane group of the SAM is $p1$, imparting local organizational chirality to the SAM; there is no global organizational chirality, however, as equal areas of (highly distinct) SAM domains form based upon the two possible spatial orientations of the $(2\sqrt{7} \times \sqrt{7})-2$ surface cell. Because of the adsorbate's bulk, adatom-bound motifs cannot be formed and the adsorbates bind to FCC sites of the gold lattice. One binds upright with a $\sim C_3$ axis and thus has achiral binding; the other tips over slightly, imparting some chirality, but the effect is weak (the lattice is close to $(\sqrt{7} \times \sqrt{7})-1$, in which the two molecules have $\sim C_3$ axes),¹⁷ and so this chirality feature is not

Table 1. Chirality Properties of the Butanethiol SAMs on Au(111)

butanethiol isomer	coverage	lattice	plane group	adatoms/vacancies	head group(s)	carbon chirality	sulfur chirality	point chirality	chiral domains
linear L	1/3	$(3 \times 2\sqrt{3})-4$	$p1 \sim cm$	2A1V	2 × adatom syn	achiral	2×RS	local	unclear
branched B	1/4	$(8 \times \sqrt{3})-4$	$p1 \sim p2$	2A0V	2 × adatom anti	achiral	2×RR or SS	local	subtle
tertiary T	1/7	$(2\sqrt{7} \times \sqrt{7})-2$	$p1$	0A0V	2 × FCC site	achiral	–	local	distinct
chiral R ₃₀	3/10	$(10 \times \sqrt{3})-6$	$\sim pg$	2A0V	2 × adatom syn, 1 × FCC, 1 × HCP	3R and 3S	2×RS	local	no
chiral R ₂₅	1/4	$(8 \times \sqrt{3})-4$	pg	4A0V	2 × adatom syn	2R and 2S	2×RS	local	no
chiral (<i>R</i>)- C	1/4	$(4 \times \sqrt{3})-2$	$p1 \sim p2$	1A0V	1 × adatom anti	2R	SS	global	subtle
chiral (<i>S</i>)- C	1/4	$(4 \times \sqrt{3})-2$	$p1 \sim p2$	1A0V	1 × adatom anti	2S	RR	global	subtle

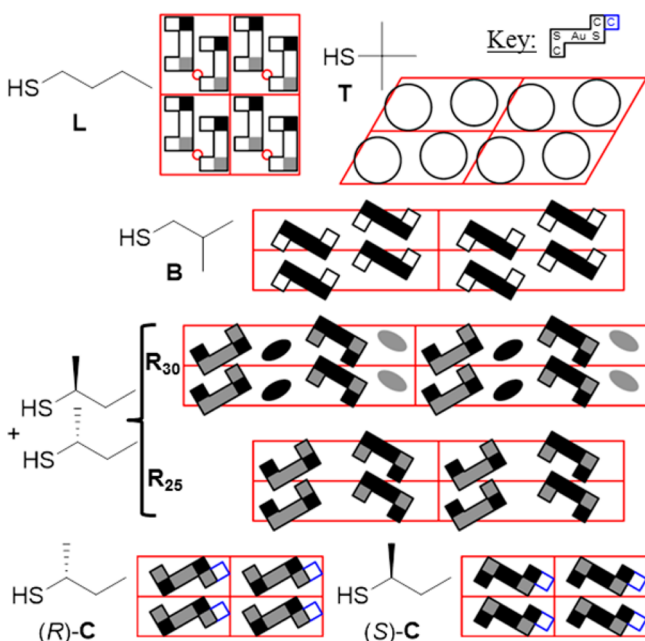


Figure 5. Sketches of four replicas of the surface cells of single domains within the butanethiol SAMs on Au(111), see Table 1. Black square and rectangular shapes depict the structure and chirality of C–S–Au–S–C units (see key), while circular and elliptical shapes depict adsorbates directly bound to Au(111) and blue squares indicate horizontally oriented ethyl groups. Shaded regions indicate either *R* (gray), *S* (black), or achiral (white) carbon, sulfur, or gold-adatom centers. Red circles indicate local vacancies.

indicated in Figure 4. The observed distinct chiral domains arise from the organization of essentially achiral adsorbates.

The linear butanethiol **L** packs tightly into the $(3 \times 2\sqrt{3})-4$ lattice at 1/3 coverage. While the adatom complexes take on the racemic *RS* (syn) conformation of the sulfur atoms, chirality is imparted by the internal arrangement of two adatom complexes and a local vacancy into the surface cell. Its plane group is $p1$, a chiral group, but without the local vacancy, a property that little affects the SAM properties, and with a small translation of the adatoms, this would become the achiral cm plane group. Observed STM images do not show distinct chiral domains.¹⁴

Two adatom motifs also pack into the unit cell of the branched chain achiral butanethiol **B** in the $(8 \times \sqrt{3})-4$ lattice at an intermediary coverage of 1/4. All four sulfur atoms take on the same chirality, but the spacings between the adatom motifs are slightly irregular, and so the plane group is $p1$ rather than $p2$. Naively, distinct chiral domains are expected for this butanethiol, but the observed STM images assemble spots in a

linear fashion along a direction that is $<5^\circ$ from a lattice vector, making domains difficult to identify.^{15,16}

In the present work we show that the SAMs of the enantiomerically pure chiral branched-chain butanethiol **C** are very similar to those of **B** except that the two adsorbate complexes per cell in **B** have become translationally equivalent. Syn adatom complexes are produced in both cases, but while **B** forms equal amounts of domains with *RR* and *SS* configurations, (*R*)-**C** forms a single domain in which the sulfur atoms take on the *SS* configuration, while (*S*)-**C** forms a single domain in which the sulfur atoms take on the *RR* configuration. The SAMs of **C** thus take on both global point chirality and global organizational chirality, the strongest-possible expression of monolayer chirality.^{1–5} However, this expectation is not strongly manifest in the STM images (see, e.g., Figure 1) as the bright and dark spots are oriented parallel to a supercell lattice vector. For example, it is not clear that the domains highlighted by the cyan circle in Figure 1 are related by reflection symmetry, manifesting global chirality, or just by rotation symmetry. Other properties of these or related SAMs (e.g., catalysis properties of SAMs made including substitution of the terminal methyl group) could more significantly reflect the intrinsic chirality, however.

The minor phase **R**₂₅ formed from a racemic mixture of (*R*)-**C** and (*S*)-**C** replaces the two homochiral molecules on each atom with a heterochiral pair without density change, producing an achiral SAM of pg plane-group symmetry. However, the major phase **R**₃₀ shows very complex chirality.¹⁸ The observed STM images take the shape of interleaving stripes each containing three adsorbate molecules, with each stripe being the mirror image of the next, implying the achiral pg plane group, but small deviations from this pattern can sometimes be discerned. Interweaving of the $3 \times R$ and $3 \times S$ molecules that fill its $(10 \times \sqrt{3})-6$ surface cell increases the coverage from 1/4 for the pure enantiomers and **R**₂₅ to 3/10. This interweaving occurs both through the simultaneous binding of *R* and *S* molecules to each adatom and through the mixing of adatom-bound and surface-bound motifs into the one surface cell. While molecules of **T** take on a circular appearance when directly bonded to Au(111), 2-butanethiol molecules appear elliptical and so bind chirally to the surface. Each surface cell thus contains 12 internal chiral elements, these two plus five from each of the adatom complexes. Despite this vast array of chiral binding sites within each surface cell, the overall SAM appears essentially achiral to the STM tip.

5. CONCLUSIONS

The butanethiol SAM domains **L**, **B**, **C**, **R**₂₅, **R**₃₀, and **T** manifest chirality on Au(111) in very different ways. The most striking external manifestation found are the distinct domains

observed for T, but these arise despite the absence of any chiral center within its surface cell. Conversely, R₃₀ contains 12 chiral centers per cell but produces an essentially achiral SAM. Further, chiral manifestations of the only system possessing global point chirality and global organizational chirality, C, are weakly depicted by STM, as they are for B, a molecule with distinct local point chirality; internal pseudo-symmetry planes also essentially destroy chirality for L.

Even though the butanethiol family contains the smallest unsubstituted chiral alkanethiol, steric interactions between the ligands rather than the headgroup always appear to be the dominant factor controlling SAM chirality. The dramatic differences found between enantiomerically pure 2-butanethiol and the major racemate domain R₃₀ show how steric packing determines the nature of the headgroup interaction, selecting among a wide range of possible structural motifs. If adatom motifs are selected, then this headgroup enforces symmetry relationships between two of the adsorbate molecules. Often an anti structure with $\sim C_2$ symmetry results, the most common packing motif found for SAMs made from individual adsorbate molecules not bound together through a mutual headgroup.² However, this headgroup also stabilizes the related syn structures with $\sim C_s$ symmetry that are far less common but typically achiral. All surface cells for butanethiol SAMs formed using this headgroup also have rectangular shape, reducing organizational aspects of chirality, and none of these led to clearly identifiable SAM chiral domains. The fundamental nature of this headgroup thus has a profound influence over the extent to which manifestations of chirality are expressed.

However, when formation of the adatom headgroup is sterically inhibited, as observed for tertiary butanethiol, SAMs with readily identifiable chiral domains result. Manipulation of headgroup structure can thus be used to influence chiral recognition in alkanethiol SAMs. This manipulation can also be used to control surface pitting, as the direct binding of ligands to the Au(111) surface produces regular, pit-free surfaces. Other known SAMs involving direct substrate binding include those of cysteamine (SHCH₂CH₂NH₃⁺) in aqueous solution, for which the tailgroup interactions control the SAM structure.^{66,67} Because of their regularity, SAMs of this type are especially significant for technological applications, and their ability to produce large chiral domains provides another feature of significant interest. Unless the SAM has global point chirality, grain boundaries and defects will always facilitate racemization, however, and so the useful lifetime of the SAM is an issue that would have to be addressed. Our images show locking of asymmetric structures on the STM time scale, but this is very short compared to that expected for a commercially useful material.

■ ASSOCIATED CONTENT

■ Supporting Information

Full details of the synthesis, characterization, electrochemistry, STM imaging, computational methods, energetics, and optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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