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Scanning Tunneling Microscopy of Prochiral Anthracene Derivatives on Graphite: Chain Length Effects on Monolayer Morphology

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Abstract: The morphology of monolayers formed upon adsorption of prochiral 1,5-substituted anthracene derivatives on highly oriented pyrolytic graphite is investigated using scanning tunneling microscopy at the liquid−solid interface. The adsorption orientation of these prochiral anthracene derivatives positions one of their enantiotopic faces in contact with the graphite. The molecules adsorb in rows with contact between adjacent anthracenes. The anthracene side chains extend perpendicular to the direction of the row repeat. All molecules within a single row adsorb via the same enantiotopic face. Anthracenes with side chains containing an even number of non-hydrogenic atoms (C, S) form monolayers in which molecules in adjacent rows adsorb via opposite enantiotopic faces. Anthracenes with side chains that contain an odd number of non-hydrogenic atoms form two-dimensional chiral domains in which all rows contain molecules adsorbed via the same enantiotopic face. This chain length effect on monolayer morphology represents a generalized example of structural effects previously observed in alkanoic acid monolayers formed on HOPG. The variation of the STM current with position in the vicinity of the anthracenes indicates that the highest occupied molecular orbital is the predominant mediator of tunneling for the aromatic group.

Introduction

Two atoms or faces in an achiral molecule are enantiotopic if they are interchanged by the action of a symmetry plane, a center of symmetry, or an alternating axis of symmetry but are not interchanged by the action of a simple symmetry axis.[1] Achiral molecules with enantiotopic atoms or faces are termed prochiral. An achiral reagent that complexes to or reacts with one of the enantiotopic groups destroys the symmetry element and creates a racemic product mixture. Resolution of racemates into pure enantiomers requires additional chiral elements. Spontaneous resolution of racemic mixtures, yielding equal amounts of enantiomerically pure crystals (a conglomerate), is an uncommon[1b] but fascinating and potentially useful phenomenon.[2] In conglomerate formation, the additional chiral element that promotes resolution is a second molecule of the same enantiomorph. In conglomerates, packing of one stereoisomer with copies of itself is thermodynamically more favorable (or kinetically faster) than packing with mirror image molecules.[3]

Adsorption of a prochiral molecule to an achiral surface creates a racemic adlayer if the adsorption geometry establishes different interactions between the two (formerly) enantiotopic groups and the surface. Interconversion of the adlayer "enantiomers" requires disruption of the surface−group interactions.[4] If the adlayer is ordered (i.e., a self-assembled monolayer), various stereochemical morphologies are possible. Chiral domains with chiral unit cells (the 2D analogue of conglomerates) form when interactions between identical 2D enantiomorphs are more favorable than between opposite 2D enantiomorphs. Mixed domains with unit cells containing both enantiomorphs (the 2D analogue of a racemic compound) form when interactions between opposite isomers are more favorable.[5,6]

In this article, scanning tunneling microscopy (STM) is used to determine the stereochemical morphology of monolayers formed from prochiral 1,5-bis-(3′-thiaalkyl) anthracenes on highly oriented pyrolytic graphite (HOPG). The morphology switches from a 2D racemate to a 2D conglomerate by the addition of a single methylene unit to each side chain. The high


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(1) (a) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; p 159. (b) About 5−10% of racemic organic compounds crystallize as conglomerates. See: ref 1a, pp 160, 300 and Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley-Interscience: New York, 1981; p 58.
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(3) Reference 1, chapters 6.1−6.4.

(4) Rabe, J. P.; Buchholz, S. *Phys. Rev. Lett.* **1991**, *66*, 2096.
(5) The unit cell of a racemic compound contains exactly one molecule of each enantiomorph. Disordered monolayers containing a 1:1 mixture of the enantiomers but with no single composition of the unit cell are the 2D analogue of a 3D pseudoracemate. Reference 1, chapter 6.3.
(6) For recent studies of adsorption induced chirality, see refs 12−14 and (a) De Feyter, S.; Gesquiere, A.; Wurst, K.; Amabilino, D. B.; Veciana, J.; De Schryver, F. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 3217. (b) Barth, J. V.; Weckesser, J.; Trimarchi, G.; Vladimirova, M.; De Vita, A.; Cai, C.; Brune, H.; Guenter, P.; Kern, K. *J. Am. Chem. Soc.* **2002**, *124*, 7991. (c) Li, C.-J.; Zeng, Q.-D.; Wang, C.; Wan, L.-J.; Xu, S.-L.; Wang, C.-R.; Bai, C.-L. *J. Phys. Chem. B* **2003**, *107*, 747. (d) Kim, B.-I.; Cai, C.; Deng, X.; Perry, S. S. *Surf. Sci.* **2003**, *538*, 45.

Scheme 1. Structures of 1,5-Bis-(3′-thia-tetradecyl) Anthracene (**1**) and 1,5-Bis-(3′-thia-pentadecyl) Anthracene (**2**)[a]
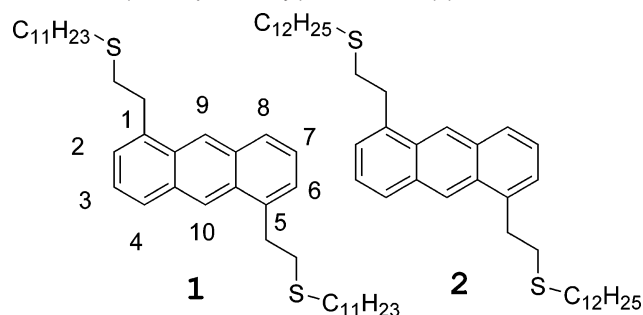
[a] The numbering convention for anthracene is presented with molecule **1**.

STM contrast of sulfur atoms and of the anthracene group makes the morphology change with chain length readily apparent and allows facile determination of the enantiotopic face in contact with the HOPG. The monolayer morphology and dependence on chain length may be of use in surface patterning applications.[7] The spatial variation of the tunneling current (height) in the vicinity of the anthracene group is remarkably similar to the spatial distribution of the molecule's highest occupied molecular orbital. Tunneling through anthracene appears to be mediated predominantly by its HOMO.

Experimental Section

Methods. A Nanoscope III scanning tunneling microscope (Digital Instruments) operating under ambient conditions at 18 °C was used to perform these measurements. Images were collected at the liquid–solid interface by adding $5-10$ μL of solution to the freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics, ZYB Grade) immediately adjacent to the STM tip. Imaging commenced within 5 min. The tip was prepared by cutting a 0.25-mm diameter platinum/rhodium (87/13) wire (Omega).

Images displayed here were obtained in constant current mode with a bias voltage of -0.8 V (sample at negative bias) and a tunneling current of $250-300$ pA. The relative separation between the STM tip and the surface is color-coded. Pink (bright) indicates topographically higher regions of the monolayer (tip withdrawn from the surface) and black (dark) corresponds to topographically lower regions. Molecular orbitals were calculated at the RHF/6-31G**//AM1 level using TITAN.[8] CPK models were derived from MMFF calculations.

Materials. The preparations of 1,5-bis-(3′-thia-tetradecyl) anthracene and 1,5-bis-(3′-thia-pentadecyl)anthracene are described in the Supporting Information. The compounds were dissolved in phenyloctane (Aldrich) and diluted to final concentrations of ∼0.15 mg/mL.

Results

1,5-Bis-(3′-thia-tetradecyl)anthracene (1). The two anthracene derivatives investigated here contain linear side chains at the anthracene 1 and 5 positions (Scheme 1). The side chains of **2** have one additional CH$_2$ group compared to **1**.

Figure 1 displays a 12 nm × 12 nm section of a monolayer formed from **1**. The bright regions of the monolayer appear as parallel rows (from lower left to upper right) with two distinct
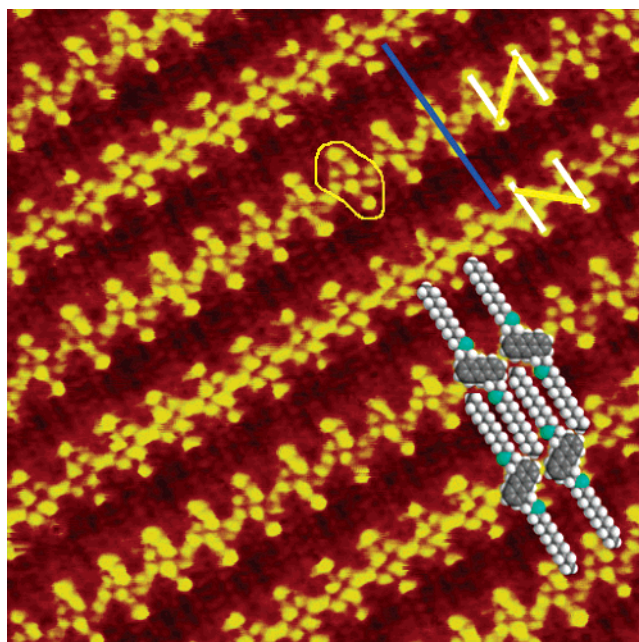
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(8) *Titan*, version 1.0.5; Wave function Inc.: Irvine, CA, 2000.

Figure 1. A 12×12 nm^2 constant current STM image of **1** adsorbed onto HOPG at -0.8 V (sample negative) and 280 pA. CPK models of **1** (sulfur atoms appear green) superimposed on adjacent rows of the image confirm adsorption via opposite enantiotopic faces. The blue bar indicates the length of one molecule. White bars indicate the S−S distance in a single molecule. The overlapping white and yellow bars indicate the forward and backward N-shape referred to in the text. The "circled" region displays the eight-circle pattern.

repeat patterns. Starting from the upper left, the odd rows appear as a series of fused backward capital N's, whereas the even rows appear as a series of fused forward capital N's. Each row is formed from a repeating pattern of eight circles, with six circles positioned like a number six domino and the remaining two circles appearing on opposite ends and edges of the six-domino, adjacent to two of the six circles. This description is easier to visualize in the "backward N" rows where the number six domino is horizontally aligned (see Figure 1). The "number six dominos" are assigned to the anthracene groups, and the peripheral circles are assigned to the sulfur atoms in the chains. The darker regions between the bright rows contain parallel rows of five or six red spots (from upper left to lower right). These rows are assigned as the hydrogens of the 3′-thiatetradecyl chains. The length of one molecule is 3.98 nm (blue bar in Figure 1), in fair agreement with the 4.16 nm distance calculated for **1** in an all *s*-trans configuration.[8] The S−S separation within a single molecule (1.31 nm, white bars) matches the 1.31 nm distance predicted by molecular mechanics and ab initio methods. CPK models of **1** are displayed as an overlay in the lower right corner of Figure 1. The models illustrate that adsorption proceeds via opposite enantiotopic faces for molecules in adjacent rows. **1** adsorbs on HOPG to form a 2D racemic monolayer with *pg* plane group symmetry.[9]

1,5-Bis-(3′-thia-pentadecyl)anthracene (2). Figure 2 displays an 11 nm × 11 nm section of a monolayer formed from **2** on HOPG. In sharp contrast to **1**, all the bright rows in this image exhibit the same repeat pattern: six bright dots (pink) positioned as a vertical number six domino, with one bright dot (pink) adjacent to the lower right edge of the domino and one less
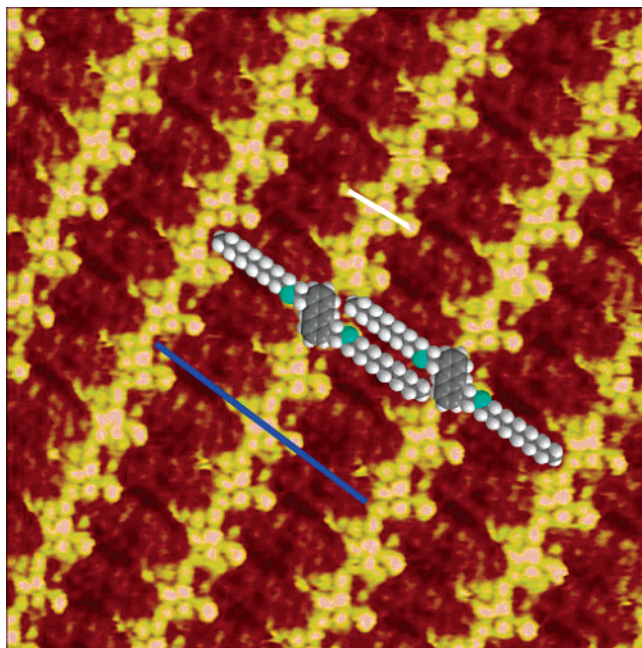
(9) Stroz, K. *Z. Kristallogr.* **2003**, *218*, 642.

Figure 2. An 11 × 11 nm² constant current STM image of **2** adsorbed onto HOPG at −0.8 V (sample negative) and 270 pA. CPK models of **2** (sulfur atoms appear green) superimposed on adjacent rows of the image confirm that all molecules in this region adsorb via the same enantiotopic face. The blue bar indicates the length of one molecule. The white bar indicates the S−S distance in a single molecule.

intense dot (green) adjacent to the upper left domino edge. The darker regions between the bright rows consist of parallel rows of orange spots (from upper left to lower right). The number of orange spots in each row is difficult to evaluate uniformly across this image. These orange spots are assigned as hydrogen atoms of the alkyl chains. The six bright dots of the domino are assigned to the anthracene. The peripheral bright (pink) and less bright (green) spots adjacent to the anthracenes are assigned to the sulfur atoms. The S−S separation (1.31 nm, white bar) is in good agreement with the 1.31 nm distance determined by calculation. The length of one molecule (4.43 nm, blue bar) is also in good agreement with the 4.40 nm distance calculated for **2** in an all *s*-trans configuration. All the molecules in this region of the monolayer adsorb to the HOPG via the same enantiotopic face. Other regions of this monolayer (not shown) consist entirely of **2** adsorbed via the other enantiotopic face. **2** adsorbs on HOPG to form a 2D conglomerate monolayer with *p*2 plane group symmetry.[9]

Discussion

Chain Length Influence on Monolayer Morphology. The monolayer formed upon absorption of anthracene derivative **1** or **2** to HOPG consists of parallel rows with interdigitating alkyl chains. Within a single row, the S atoms define a line on either side of the anthracene core. The repeat distance along this line is 11.2 Å for **1** and 11.3 Å for **2**. The anthracene cores of adjacent molecules within a single row are in van der Waals contact, aligned parallel to each other and rotated by 22° (anthracene long axis) from the line of S atoms. The sense of rotation (CW vs CCW) alternates between adjacent rows in the monolayer formed from **1** but remains the same (at least within a single domain) in the monolayer formed from **2**.

Compounds **1** and **2** are prochiral structures with C_{2h} symmetry. Adsorption to HOPG via one of the molecule's

enantiotopic faces generates one of two possible 2D molecule-surface enantiomers. Although isolated mirror image 2D enantiomers have identical energy, pairs of interacting 2D isomers are diastereomeric and have distinct energies. For both **1** and **2**, the lowest energy monolayer is composed from rows containing a single 2D enantiomer. For **1**, the lowest energy monolayer contains opposite 2D enantiomers in adjacent rows. For **2**, the lowest energy monolayer is composed of regions with the same 2D enantiomer in every row.

Surface−adsorbate and adsorbate−adsorbate interactions determine monolayer morphology.[10−13] In the absence of bonds between adsorbates (e.g., hydrogen bonding) or between the surface and adsorbates (thiols on gold), adsorbate packing considerations and polar effects play important roles. *n*-Alkanes and various terminally functionalized *n*-alkanes form ordered monolayers at the HOPG−phenyloctane interface. The methylene groups and C−C bonds of adjacent alkyl chains align in registry so as to maximize interadsorbate van der Waals interactions.[11] Adsorbates with long alkyl chains can effect this alignment with various separations of neighboring rows.

The CPK models of **1** and **2** superimposed on their respective STM images indicate that the terminal CH_3 group of an alkyl chain from one row is in registry with the 2′-CH_2 groups of the neighboring alkyl chains from the adjacent rows (Scheme 2, red CH_2 and CH_3 groups). This orients the terminal CH_2−CH_3 bond of one molecule (Scheme 2, green) parallel to the C_{aryl}−C1′ bond (blue) of molecules in the adjacent row. The different stereomorphologies observed for **1** (2D racemic compound) and **2** (2D conglomerate) arise from the different relative orientations of the CH_2−CH_3 and C_{aryl}−C1′ bonds **within the same side chain**. These two bonds are parallel in **2**. Consequently, the C_{aryl}−C1′ bonds of anthracenes in adjacent rows are parallel, and neighboring rows contain molecules adsorbed via the same enantiotopic face (Scheme 2). By contrast, the presence of one fewer methylene in the side chains of **1** leads to an angle of ∼110° between the CH_2−CH_3 and C_{aryl}−C1′ bonds within the same side chain. The C_{aryl}−C1′ bonds of anthracenes in adjacent rows form a similar angle. With all *s*-trans side chains, the optimal alkyl chain registration is attained only if molecules in adjacent rows adsorb via opposite enantiotopic faces (Scheme 2).

The stereomorphology of *n*-alkanoic acid monolayers on HOPG depends on carbon chain length.[12] Acids with even numbers of carbons form conglomerate domains constructed from a single 2D enantiomer. Acids with odd numbers of carbons form racemic domains with both 2D enantiomers present in the unit cell. In both cases, the monolayer building blocks are the hydrogen-bonded acid dimers. Although the acid monomers exhibit C_s symmetry, the acid dimers possess C_{2h}

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Scheme 2. Stick Figure Representation of the Side Chain and Anthracene Orientations within the Interdigitated Rows of **1** (Left) and **2** (Right)[a]
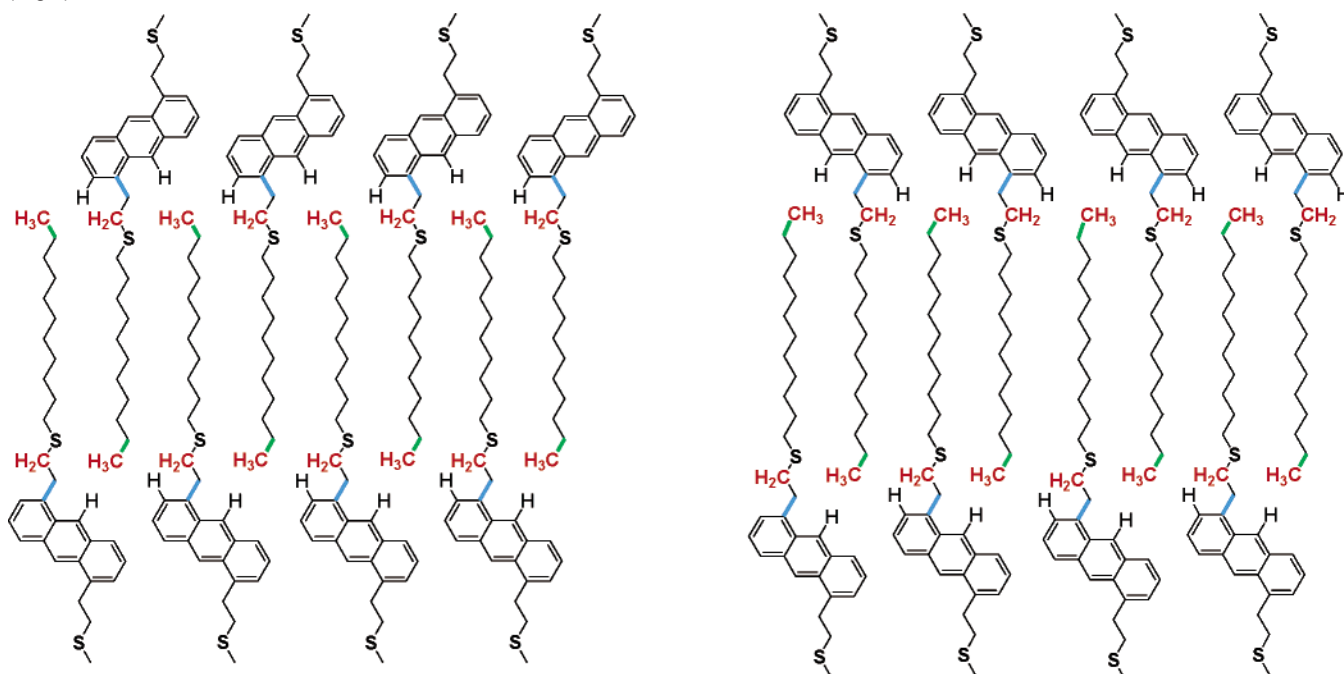
[a] Terminal CH$_3$ group and 2′-CH$_2$ groups are indicated in red. The terminal CH$_2$−CH$_3$ bond within each chain (green) is parallel to the C$_{aryl}$−C1′ bonds (blue) of molecules in the adjacent row. The parallel alignment of the CH$_2$−CH$_3$ and C$_{aryl}$−C1′ bonds within the same side chain of **2** translates into parallel alignment of C$_{aryl}$−C1′ bonds of anthracenes in adjacent rows and to monolayers containing a single 2D enantiomer. The 110° angle between the CH$_2$−CH$_3$ and C$_{aryl}$−C1′ bonds within the same side chain of **1** produces a similar angle between the C$_{aryl}$−C1′ bonds of anthracenes in adjacent rows. Monolayer formation with **1** requires molecules in adjacent rows to adsorb via opposite enantiotopic faces.

symmetry, the same as the anthracene derivatives investigated here. One can visualize the acid dimer as a "headgroup" analogous to the anthracene. From this vantage point, two odd carbon side chains appended to the dimer headgroup generate a chiral 2D morphology. Two even carbon side chains appended to the dimer headgroup produce a racemic morphology with opposite 2D enantiomers constituting adjacent rows. The chain length dependence of monolayer morphology for carboxylic acid dimers is directly analogous to that observed for anthracenes **1** and **2**.

Chemical Marker Groups. The presence of high tunneling, "chemical marker groups"[13] at strategic positions within alkanoic acids greatly enhances visualization of chain length influence on monolayer morphology.[14] For example, the stereomorphology of a monolayer prepared from α-bromoalkanoic acids is readily determined from the relative placements of two pairs of bromine atoms in adjacent rows. The sulfur atoms and anthracene group within **1** and **2** likewise function as chemical markers and morphology reporters. Starting at any sulfur, an arrow drawn toward the central lobe of the anthracene on the same long edge of the molecule defines a motion, clockwise or counterclockwise, around the anthracene (Figure 3, blue arrows). The sense of the arrow defines which 2D enantiomer is present.

Close inspection of the STM images from **1** and **2** indicate that the central two spots of the anthracene groups (the "six dominos") are higher and more widely spaced than the two pairs of spots on either side. The spatial distribution of the tunneling "height" bears remarkable similarity to the wave function of the HOMO calculated for an isolated molecule of **1** (overlay,

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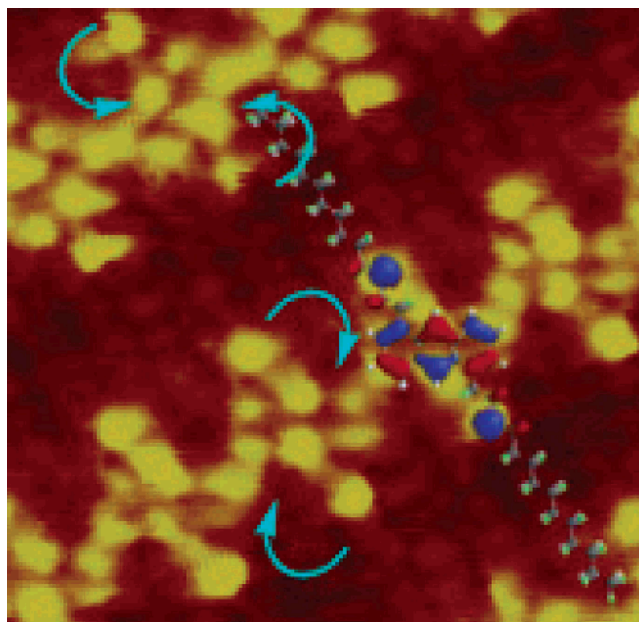
Figure 3. A magnified section of the constant current STM image of **1** adsorbed onto HOPG (from Figure 1). The spatial distribution of the HOMO (six central red and blue lobes) and the highest occupied sulfur containing MO (blue lobes above and below the six HOMO lobes) are displayed superimposed on a ball-and-stick model of **1**. The blue arrows start at sulfur, pointing away from the anthracene, and curve back to the nearest central lobe of the anthracene. The sense of the arrow (top row: counterclockwise, bottom row: clockwise) identifies which enantiotopic face of **1** is adsorbed to the HOPG.

Figure 3). This HOMO contains six lobes, with the two largest centered on the middle anthracene carbons (C9 and C10, see Scheme 1 for numbering). The other four lobes span C1−C2,

C3−C4, C5−C6, and C7−C8. The gas-phase ionization potential of the anthracene-derived HOMO, 7.0 eV, places it 1.3 eV closer to the graphite Fermi level than the next highest orbital (HOMO −1). The latter molecular orbital is also localized on anthracene but consists of four elongated lobes (three vertical nodes and no horizontal nodes for the overlay orientation shown in Figure 3). The anthracene LUMO exhibits small lobes at C9 and C10, lobes that extend across C2 and C3 (C6 and C7), and large lobes that extend across C1, C1a (the quaternary carbon between C1 and C9), C4a, and C4.

The images of **1** and **2** suggest that tunneling at anthracene is mediated primarily by its HOMO.[15] Comparable patterns are observed from **1** on HOPG at positive sample bias (+0.7 V, see Figure S1 in Supporting Information). STM patterns of anthracene adsorbed to metals are distinctly different.[16] STM images of anthracene on Ag(110) in UHV at 50 K, positive sample bias, and low gap resistance (+1.2 V, 15.4 nA, 78 MΩ) resemble the molecule's LUMO.[16a] Structureless ellipsoidal shapes are observed at higher gap resistance (1 V, 100 pA). Negative sample bias yields bilobed patterns on Ag(110) in UHV. STM images of anthracene adsorbed to Rh, Cu, and Ag in aqueous solution exhibit a variety of patterns, none of which evokes the anthracene HOMO or LUMO.[16b−d] Tunneling patterns and bias dependences clearly vary with substrate, environment, and gap resistance. The origin of these differences is, as of yet, incompletely understood.

The highest occupied molecular orbital with significant amplitude at the sulfur atoms (Figure 3) has a gas-phase ionization potential of 8.9 eV. At negative sample bias (−0.7 V), the sulfur atoms appear slightly taller than the central two lobes of the anthracene. At positive bias, (+0.7 V), the sulfur atoms and central anthracene peaks appear with similar heights. Both topological and electronic factors determine apparent STM heights. The larger radius of sulfur compared to carbon is at least partly responsible for the relative heights observed in these STM images.

Conclusion

The number of heavy atoms in the side chains of prochiral anthracene derivatives **1** and **2** determines the morphology of their self-assembled monolayers on HOPG. The molecules adsorb in rows, with contact occurring between the 3,4 and 7,8 positions of adjacent anthracenes. The anthracene side chains at the 1 and 5 positions extend roughly perpendicular to the direction of the row repeat. All molecules within any one row adsorb to HOPG via the same enantiotopic face. Side chains containing an even number of carbon plus sulfur atoms promote the formation of monolayers in which neighboring rows contain anthracenes adsorbed via opposite enantiotopic faces. Such monolayers are the 2D analogues of racemic compounds. Side chains containing an odd number of heavy atoms promote the formation of monolayer domains in which all rows consist of anthracenes adsorbed via the same enantiotopic face. These monolayers are the 2D analogues of 3D conglomerates. The change of monolayer morphology from **1** to **2** represents a generalized example of chain length effects that have been extensively investigated for alkanoic acid monolayers on HOPG. The hydrogen-bonded carboxylic acid dimer and the anthracene core fulfill comparable structural roles in the two systems.

Structural properties of these monolayers (interdigitation of alkyl chains on both sides of a headgroup, large domain sizes, odd−even effects) combined with facile morphology determination via the anthracene and sulfide groups make this a good system to identify side-chain motifs that promote monolayer patterning. An anthracene substituted with one 14 and one 15 heavy atom side chain is a simple example. If the thermodynamically preferred assembly segregates side chains by length, the racemic monolayer that results should exhibit two adjacent rows composed from the same 2D enantiomer adjacent to two rows containing the opposite 2D enantiomer.[17] If interdigitation of 14 and 15 heavy atom side chains is more favorable, a conglomerate monolayer will form. Surveys of extended monolayer sections will allow rapid quantification of the two morphologies and their relative thermodynamics. A wide variety of side-chain interactions may be studied with this approach.[7a,b]

Supporting Information Available: Synthetic schemes and spectral data (^{1}H NMR and ^{13}C) for **1** and **2** and a single STM scan of **1** on HOPG recorded at three different bias voltages (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The unit cell should contain four molecules from four adjacent lamellae.