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Rigid Molecular Tripod with an Adamantane Framework and Thiol Legs. Synthesis and Observation of an Ordered Monolayer on Au(111)

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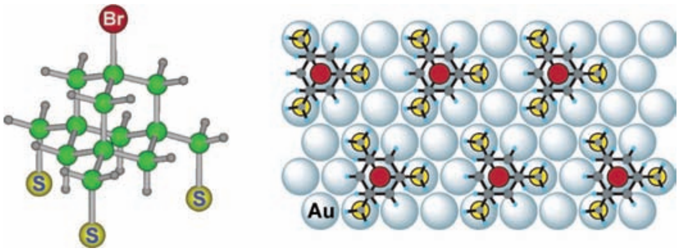

Tripod-shaped trithiols **1**−**3**, containing CH_2SH groups at the three bridgehead positions of the adamantane framework and a halogen-containing group [Br (**1**), *p*-BrC_6H_4 (**2**), or *p*-IC_6H_4 (**3**)] at the fourth bridgehead, were synthesized, and self-assembled monolayers (SAMs) were prepared on atomically flat Au(111) surfaces. The three-point chemisorption of these tripods was confirmed by polarization modulation infrared reflection absorption spectroscopy, which showed the absence of a S−H stretching band. Scanning tunneling microscopy of the SAM of **1** exhibited a hexagonal arrangement of the adsorbed molecule with a lattice constant of 8.7 Å. A unidirectionally oriented, head-to-tail array of **1**, which allows the close approach of neighboring molecules, is proposed as a reasonable model of the two-dimensional crystal, where the adsorbed sulfur atoms form a quasi-($\sqrt{3} \times \sqrt{3}$)R30° lattice. The charge of the electrochemical reductive desorption of the SAM of **1** was in good agreement with the expected surface coverage, while the SAMs of **2** and **3** showed somewhat less (ca. 70%) charge. The large negative reduction peak potentials, observed for the SAM of **1**, are taken to indicate a tight anchoring of this tripod by three sulfur atoms.

Introduction

Thiols and disulfides have a strong tendency to be chemisorbed to a gold surface, forming self-assembled monolayers (SAMs).[1] The importance and utility of the spontaneous formation of tight S−Au bonds has attracted a great deal of interest in recent years, since it is an effective approach for the construction of a variety of functional molecular assemblies, including unimolecular electronic devices[2−9] and molecular machines.[10−13] One of the requirements for such applications is the appropriate design of the anchoring point, which ensures a fixed angle of the adsorbed molecule relative to the gold surface and sufficient molecular separation to avoid possible undesirable intermolecular interactions. Tripod-shaped mol-

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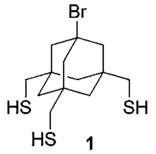
ecules, having three legs and a binding group at each end of the legs, are strong candidates for satisfying such a requirement. It would, therefore, be of interest to determine if it is possible for such a molecule, especially one with three SH groups, to serve as a rigid anchor in the construction of highly ordered SAMs. Several molecular tripods with three surface-binding legs have been synthesized using the tetrahedral configuration of sp^3-hybridized carbon[14−20] or silicon[12,21,22] atom as a core structural component. Other tripods have utilized adamantane, in which the four bridgehead bonds have a tetrahedral orientation.[16,17,23−26] Despite the well-defined geometry of these tripods, it appears rather difficult to obtain a monolayer of such molecules with a highly ordered, two-dimensional structure, due to insufficient van der Waals interactions between neighboring molecules, an important factor in self-assembly, and to the increased freedom of orientation of each triangular molecule compared to rodlike monothiols. To the best of our knowledge, the observation of the ordered SAM of a tripod shaped molecule has not been reported.

Here, we report on the synthesis of trithiol **1** and its haloaryl derivatives **2** and **3**, in which the C−Br or C−I bond, because of the rigid adamantane framework, is fixed in a perpendicular orientation to the surface of the gold substrate. Analyses of these SAMs on Au(111) by means of infrared reflection absorption spectroscopy, scanning tunneling microscopy (STM), and cyclic voltammetry demonstrated that these molecules are indeed adsorbed to the gold surface by three sulfur atoms per molecule and that the SAM of **1**, in particular, forms a two-dimensional crystal, for which the lattice constants could be determined.



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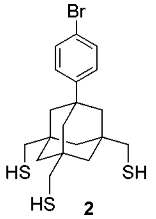

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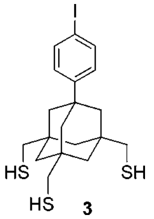

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Results and Discussion

Synthesis. Scheme 1 shows the synthetic route to tripod **1**. The photochemical carbonylation[27] of the bridgehead C−H bonds of 1-bromoadamantane gave triester **4**, which was converted to triol **5** by reduction with lithium aluminum hydride. Conversion of this primary alcohol to a chloride or bromide by treatment with $SOCl_2$, $SOBr_2$, or PBr_3 was not successful because these reactions involve nucleophilic substitution by chloride or bromide ion at the sterically congested, neopentyl-type carbon. On the other hand, the triol could be cleanly converted to the tritriflate **6**. With its excellent leaving group characteristics, all of the three CF_3SO_3 groups in **6** could be transformed to acetylthio groups by treatment with potassium thioacetate in the presence of a crown ether, which was added to enhance the nucleophilic reactivity of AcS^-. Alkaline hydrolysis of the trithioacetate **7** gave trithiol **1** as air-stable crystals.

The introduction of a 4-bromophenyl group at C-1 was achieved by the silver ion-promoted ionization of the C−Br bond of tritriflate **6** and subsequent trapping of the carbocationic intermediate with bromobenzene (Scheme 2). The three CF_3SO_3 groups of **8** were then converted to SH groups via trithioacetate **9** in a manner similar to that described above.

On the other hand, the reaction of tritriflate **6** with iodobenzene in the presence of $AgSbF_6$ was sluggish, requiring 8 weeks for a complete reaction in refluxing CH_2Cl_2. Alternatively, the 4-iodophenyl derivative **11** could be synthesized by a stepwise conversion via the phenyl derivative **10** (Scheme 3). In the iodination of **10** using $PhI(OCOCF_3)_2/I_2$,[28] a byproduct, 2,4-diiodophenyl derivative **12**, was formed, which could be separated by recrystallization. The purified monoiodo derivative **11** was similarly converted to trithiol **3** via trithioacetate **13**.

Structural Analysis. A single-crystal X-ray analysis of **1** (Figure 1a) indicated that one of the C−S bonds (C12−S2) is

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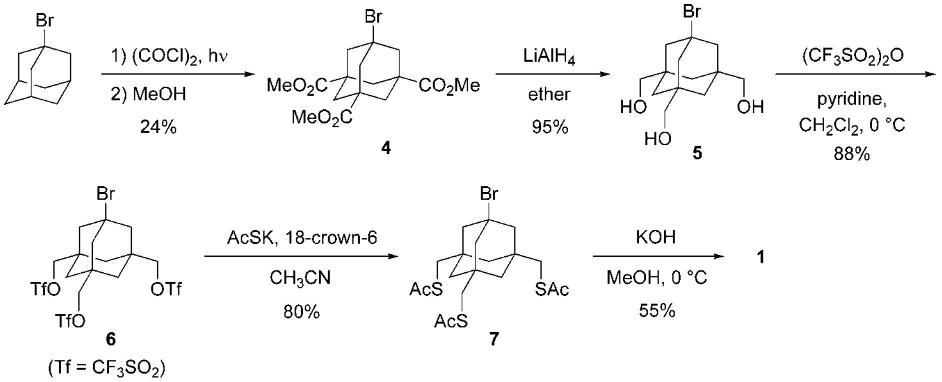
SCHEME 1. Synthesis of 1



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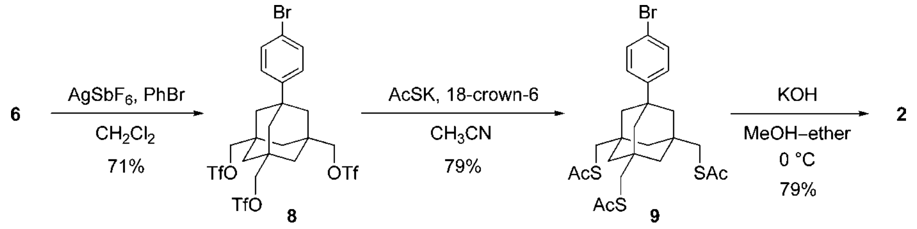
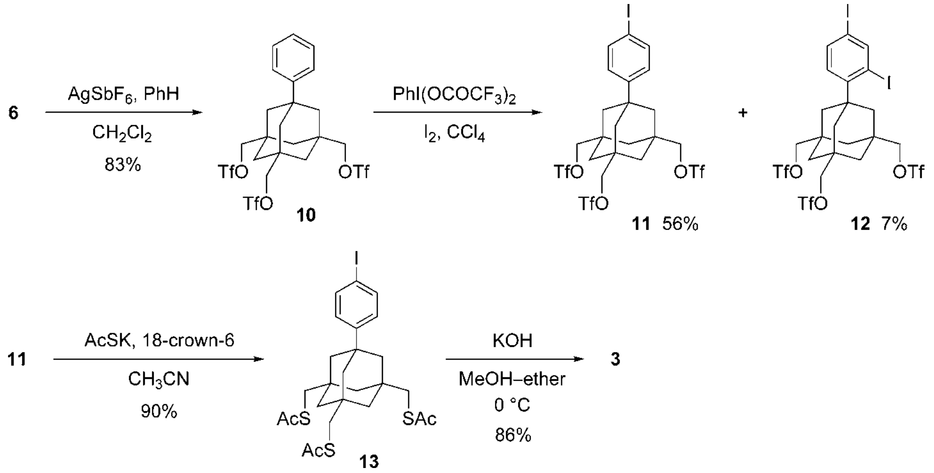


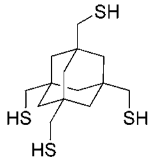
SCHEME 3. Synthesis of 3



nearly anti-periplanar to the C−Br bond, while the other two sulfur atoms, S1 and S3, adopt gauche-like conformations with respect to the C−Br bond. When a monolayer is formed on a gold substrate, the latter sulfur atoms can be oriented anti, so that the three sulfur atoms form an equilateral triangle. In such a conformation, the S−S distance would be expected to be 5.0 Å (Figure 1b), which is close to the interatomic distance observed between sulfur atoms in *n*-alkanethiol SAMs on Au(111), $\sqrt{3} \times D = 4.995$ Å (D denotes the interatomic Au−Au distance, 2.884 Å[1f]). Such features would ensure the secure three-point chemisorption of **1** without an unfavorable change in molecular geometry that could lead to increased molecular strain.

Formation of SAMs on Au(111). The SAMs of tripods **1**−**3** were formed by immersing a substrate, prepared by depositing gold on a mica sheet, in a 0.1 mM solution of one of trithiols **1**−**3** in EtOH or CH_2Cl_2 at ambient temperature. Immersion for 24 h was required for the formation of monolayers that gave reproducible voltammograms in electrochemical desorption experiments.

The three-point adsorption of trithiols **1**−**3**, with the elimination of the thiol hydrogen atoms, was confirmed by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). S−H vibrations, observed at around 2560 cm^{-1} in the transmission IR spectra of neat samples, were not detected in PM-IRRAS spectra of monolayers on gold (Figure 2). The absence of S−H absorption peaks supports the conclusion that the molecules are attached via bonding with the three sulfur atoms in a tripod-like, perpendicular orientation. This observation is consistent with the reported XPS data for the SAM of tetrathiol **14**, in which three sulfur atoms of the molecules were bonded to the polycrystalline gold surface.[23]



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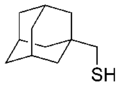

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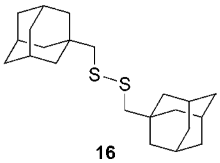

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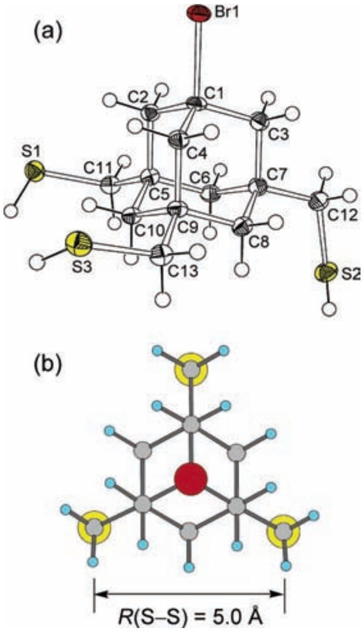

FIGURE 1. (a) ORTEP drawing of **1** as determined by single-crystal X-ray diffraction analysis at 100 K. Ellipsoids are drawn at the 50% probability level for non-hydrogen atoms. Selected angles (deg): C5−C11−S1, 117.06(16); C7−C12−S2, 116.12(18); C9−C13−S3, 117.13(17); C2−C5−C11−S1, −63.3(2); C3−C7−C12−S2, −177.30(16); C4−C9−C13−S3, 59.6(2). (b) Top view of **1**. Thiol hydrogens have been omitted. C−C−C−S torsion angles and C−C−S angles have been changed so that the C−S bonds align parallel to the C1−Br1 bond.

The antisymmetric and symmetric CH_2 stretching peaks, appearing at 2910 and 2850 cm^{-1}, respectively, in the spectra of neat samples, were shifted by 8−17 cm^{-1} to higher frequencies when the molecules were adsorbed on Au. These shifts might indicate the tightening of the C−H bonds due to the fixation of the three legs on the Au surface. The shoulders observed on the high-wavenumber side of these peaks in the SAM spectra can be ascribed to the CH_2 groups adjacent to a sulfur atom.

Scanning Tunneling Microscopy. The molecular arrangement of **1** in a monolayer on a Au(111) surface was analyzed by STM under water, using perchloric acid as the supporting electrolyte. Figure 3a shows a typical image, which can be interpreted as two overlapping periodical patterns. One consists of bright spots, and the other contains dark spots with a larger period. Each pattern could be individually visualized by frequency deconvolution using the Fourier transform method (Figure 3b).[29] Both are hexagonal close-packed lattices with nearest spacings of 2.9 and 8.7 Å, respectively. The former corresponds to the Au(111) surface,[1f] while the latter indicates that adsorbed molecules of **1** are separated by a distance equal to three times the Au−Au interatomic distance. In the raw image, the two patterns are overlapped so that the center of each molecule of **1** lies on one of the underlying Au atoms.

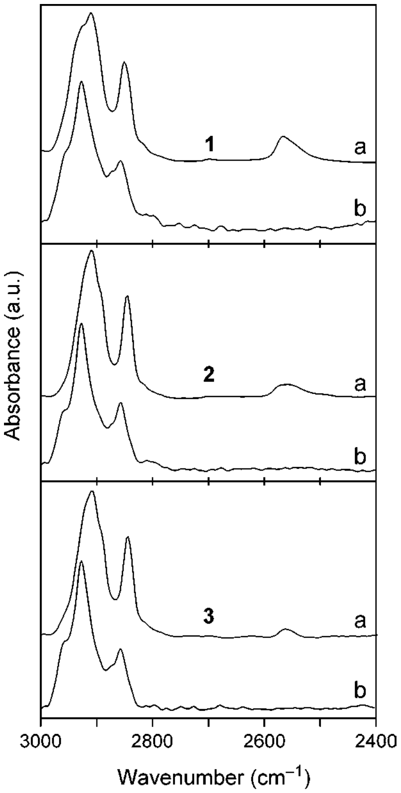

FIGURE 2. Infrared absorption spectra of trithiols **1**−**3**. (a) Transmission spectra of neat samples on a KBr plate. The sample was prepared by dropping a 5 mM solution of the compound in ethyl ether on a plate and slowly evaporating the solvent. The dropping and evaporation were repeated five times. (b) PM-IRRAS spectra of the monolayers on Au(111).

The model shown in Figure 4 represents a plausible structure. Although the orientations of individual molecules, i.e., the twist angles around the C_3 axis, were not determined, a unidirectionally oriented, head-to-tail arrangement, which allows a close approach, is considered to be a favorable model. In this model, the adsorbed sulfur atoms occupy near-atop sites of the Au lattice, forming a quasi-($\sqrt{3} \times \sqrt{3}$)R30° lattice. Note that the surface density of the adsorbed sulfur atom is identical to that for *n*-alkanethiol SAMs, irrespective of the orientation of the adsorbed molecules.

Reductive Desorption. The electrochemical behavior of thiol SAMs on gold allows the state and surface coverage of the adsorbed thiolate molecules to be examined. The cyclic voltammetry of *n*-alkanethiol monolayers on a Au(111) electrode, measured in alkaline solution, is known to exhibit a cathodic wave due to the charge produced by reductive desorption (eq 1).[30−34] The observed charge, typically 90−110 μC/cm^2 for such monolayers,[31,32,34] is significantly greater than the theoretical value, 73 μC/cm^2, which corresponds to the coverage of 7.6×10^{-10} mol/cm^2, derived from a ($\sqrt{3} \times \sqrt{3}$)R30° packing

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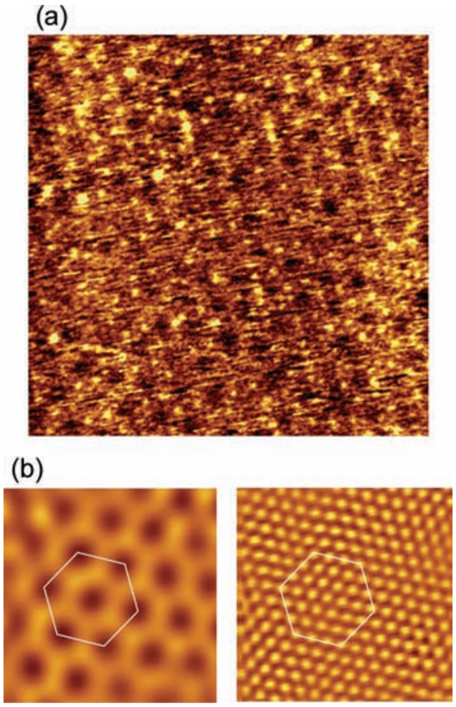

FIGURE 3. (a) STM image of the SAM of **1** on a Au(111) surface, as measured in 0.1 M aq $HClO_4$ at ambient temperature. A silver wire was used as the reference electrode. Image area 12 nm × 12 nm, setpoint current 400 pA, bias voltage 700 mV, Au electrode potential −300 mV, tip potential 400 mV. (b) Computer images of the 8.7 Å (left) and 2.9 Å (right) components of the lower left 4 nm × 4 nm area of (a). These images were obtained by inverse Fourier transform of each of the two intense frequency components obtained by two-dimensional Fourier transform of the raw image. The unit cell, indicated by hexagons, has a side length of 8.7 Å.

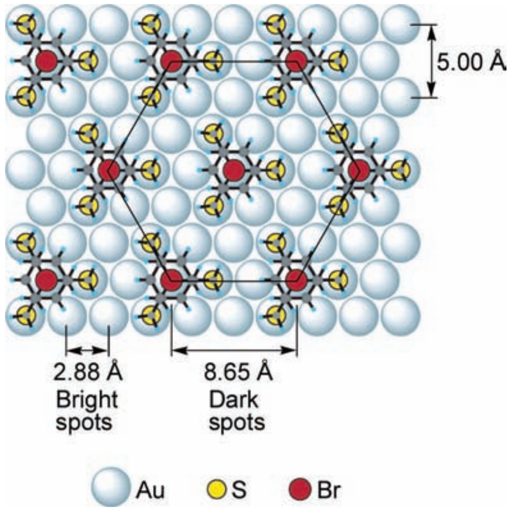

FIGURE 4. Top view of a possible arrangement of **1** for the SAM on Au(111). The unit cell is shown by a hexagon. All molecules are drawn in the same orientation to minimize unfavorable intramolecular interactions. Sulfur atoms are assumed to be located on the near-top sites.

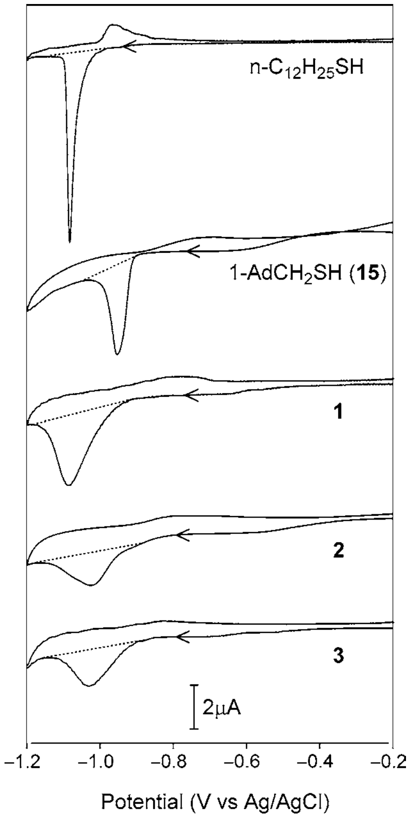

FIGURE 5. Cyclic voltammograms for the reductive desorption of SAMs derived from *n*-dodecanethiol, monothiol **15**, and trithiols **1**−**3** on Au(111) working electrode in 0.5 M KOH. Scan rate, 20 mV/s. Geometric area of the working electrode, 0.152 cm^2. The charge for reductive desorption was calculated from the area below the dotted line.

TABLE 1. Peak Potential, Full Width at Half-Maximum (fwhm), and Charge for the Electrochemical Reductive Desorption of SAMs Derived from Thiols on Au(111)

thiol	E_p (V vs Ag/AgCl)	total reductive charge[a] ($\mu C/cm^2$)	fwhm (mV)
n-$C_{12}H_{25}SH$	−1.084	100	20
1-$AdCH_2SH$ (**15**)	−0.954	72	47
1	−1.088	100	91
2	−1.026	70	129
3	−1.032	70	128

[a] Calculated by integrating the cathodic wave. Uncertainty due to sample-to-sample variations, ±10%.

structure. This difference can be attributed to the surface roughness of the Au substrate, 1.05−1.15,[34,35] and a nonfaradaic current resulting from the change in double layer charges upon removal of the adsorbed molecules.[34]

$$RS\text{-}Au + e^- \rightarrow RS^- + Au \qquad (1)$$

Figure 5 shows cyclic voltammograms for the reductive desorption of trithiols **1**−**3**, monothiol **15**,[36] and *n*-dodecanethiol adsorbed to Au(111). All exhibited an irreversible reduction wave. The peak potential (E_p), full width at half-maximum (fwhm), and reductive charge are listed in Table 1. The observed reductive charge for *n*-dodecanethiol SAM, 100 $\mu C/cm^2$, which is 1.4 times greater than expected, is in agreement with the

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(35) (a) Rodriguez, J. F.; Mebrahtu, T.; Soriaga, M. P. *J. Electroanal. Chem.* **1987**, *233*, 283. (b) Weisshaar, D. E.; Walczak, M. M.; Porter, M. D. *Langmuir* **1993**, *9*, 323. (c) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528.

(36) 1-(Mercaptomethyl)adamantane (**15**) was prepared in a three-step synthesis from 1-(hydroxymethyl)adamantane by similar transformations employed for the synthesis of **1**. See the Experimental Section.

reported values and serves as a reference for charge determination. Thus, with the assumption that the total contribution from surface roughness[37] and the nonfaradaic current is assumed to be constant at ca. 30% of the total reductive charge for all the SAMs studied, the faradaic component determined for each SAM can be taken as reflecting the surface density of the adsorbed sulfur atoms. The very small fwhm, such as that observed for *n*-dodecanethiol, has been interpreted to be the result of interchain attractive interactions between van der Waals-contacting molecules.[34]

It has been reported that, in the SAM prepared from disulfide **16**, the 1-AdCH$_2$S groups are hexagonally packed on Au(111) with a lattice constant of 6.65 Å.[38] The reductive charge observed for the SAM of **15**, 72 μC/cm^2, can be interpreted as the sum of the theoretical reductive charge (41 μC/cm^2) for the 1-AdCH$_2$S groups adsorbed in the same surface density, plus a nonfaradaic contribution. The fwhm is significantly larger than that for the *n*-dodecanethiol SAM, indicating a reduced lateral interactions between neighboring adamantane frameworks.

The SAM of trithiol **1** showed essentially the same reductive charge (100 μC/cm^2) as that of *n*-dodecanethiol SAM, which would be expected from the arrangement shown in Figure 4. The observation of a large fwhm (91 mV) indicates poor attractive interactions between neighboring molecules of **1**, which is in complete agreement with the extended (8.7 Å) intermolecular distance. Despite this result, the E_p is as negative as *n*-dodecanethiol. In general, the large negative E_p values reported for long *n*-alkanethiol SAMs have been explained by low solubility of the detached thiol as well as by the resistance of the adsorbed molecules to detachment due to strong attractive intermolecular interactions. The present results indicate that **1** is not readily desorbed despite the lack of such interactions, and are better attributed to the tight binding of **1** to the gold substrate by the three S−Au bonds.

The diminished reductive charges and large fwhms of the SAMs of **2** and **3** suggests the existence of disorder as a result of incomplete self-assembly. The degree of disorder has been reported to vary with several different factors, such as the solvent used in the preparation of the SAM[39] and the time after preparation.[40] The presence of an aromatic group in **2** and **3** may also affect the rate of two-dimensional crystallization. Note that the aromatic ring would not be expected to cause any significant intramolecular repulsion when the molecules of **2** and **3** stand upright on the Au surface. Thus, modification of the conditions for adsorption might permit the formation of a better ordered SAM.

Conclusion

In summary, molecular tripod **1** and its 4-halophenyl derivatives, **2** and **3**, were synthesized, and the formation of their SAMs on Au(111) by three-point adsorption was confirmed. STM analyses indicated a hexagonal packing with a nearest intermolecular distance of 8.7 Å for the SAM of **1**. Unlike the SAM of monothiol **15**, where the intermolecular distance is approximately equal to the van der Waals diameter of the sphere-like adamantane framework, the SAM of **1** showed a significantly greater separation between adsorbed molecules due to the spatial requirements of the three legs. The present result is to our knowledge the first example of the observation of a two-dimensional crystal composed of tripod-shaped molecules that are chemisorbed to a solid surface. The spontaneous formation of the highly ordered SAM of **1** would provide a useful end of larger functional molecules, thus enabling the vertical fixing of rod-shaped electro- and photoactive molecular components to metal surfaces with a well defined two-dimensional structure. More detailed studies of the SAMs of adamantane tripods by means of STM under ultrahigh vacuum conditions are currently underway.

Experimental Section

1-Bromo-3,5,7-tris(methoxycarbonyl)adamantane (4). A solution of 1-bromoadamantane[41] (5.00 g, 23.2 mmol) in oxalyl chloride (20 mL) was irradiated for 50 h with a 450-W high-pressure mercury lamp at room temperature using a Pyrex flask, and the oxalyl chloride was removed under reduced pressure. The tricarboxylic acid trichloride thus obtained was treated under stirring with dry methanol (50 mL) at room temperature for 3 h. Evaporation of the methanol followed by medium-pressure liquid chromatography (MPLC) (SiO$_2$, hexane−ether 1:1) afforded **4** (2.17 g, 24%) as colorless crystals: mp 123−124 °C; ^{1}H NMR (CDCl$_3$) δ 2.00 (d, J = 12.9 Hz, 3H), 2.06 (d, J = 12.9 Hz, 3H), 2.40 (s, 6H), 3.71 (s, 9H); ^{13}C NMR (CDCl$_3$) δ 37.9, 44.5, 47.9, 52.3, 59.0, 174.4. Anal. Calcd for $C_{16}H_{21}BrO_6$: C, 49.37; H, 5.44. Found: C, 49.51; H, 5.45.

1-Bromo-3,5,7-tris(hydroxymethyl)adamantane (5). A solution of triester **4** (0.773 g, 1.99 mmol) in ether (20 mL) was added to a stirred suspension of lithium aluminum hydride (0.274 g, 7.22 mmol) in ether (20 mL) over a period of 10 min. The reaction mixture was stirred at room temperature for 3.5 h, cooled on ice, and quenched by the addition of water (2 mL). The solvent was evaporated under reduced pressure, and the residue was extracted seven times with 20 mL portions of ethyl acetate. The combined extracts were evaporated to give **5** (0.574 g, 95%) as colorless crystals: mp 136−137 °C; ^{1}H NMR (CD$_3$OD) δ 1.19 (d, J = 12.0 Hz, 3H), 1.35 (d, J = 12.0 Hz, 3H), 2.04 (s, 6H), 3.25 (s, 6H), the hydroxyl protons were not observed due to rapid H−D exchange; ^{13}C NMR (CD$_3$OD) δ 40.3, 41.4, 51.5, 66.5, 72.3. Anal. Calcd for $C_{13}H_{21}BrO_3$: C, 51.16; H, 6.94. Found: C, 51.21; H, 7.05.

1-Bromo-3,5,7-tris[(trifluoromethylsulfonyloxy)methyl]adamantane (6). A solution of trifluoromethanesulfonic anhydride (2.85 g, 10.1 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise to a solution of triol **5** (0.564 g, 1.85 mmol) and pyridine (3.0 mL) in CH$_2$Cl$_2$ (20 mL) with stirring at 0 °C over a period of 10 min, and the reaction mixture was then further stirred at 0 °C for 2 h. The mixture was diluted with CH$_2$Cl$_2$ (30 mL), washed with 10% HCl and 5% NaHCO$_3$, and dried (MgSO$_4$). The solvent was removed under reduced pressure to give essentially pure **6** (1.14 g, 88%) as colorless crystals: mp 116−117 °C after purification by GPC (Japan Analytical Industry JAIGEL 1H+2H, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 1.47 (d, J = 12.3 Hz, 3H), 1.54 (d, J = 12.3 Hz, 3H), 2.16 (s, 6H), 4.22 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 37.1, 38.1, 47.6, 55.9, 81.9, 118.5 (q, $^1J_{CF}$ = 319 Hz). Anal. (after purification by GPC) Calcd for $C_{16}H_{18}BrF_9O_9S_3$: C, 27.40; H, 2.59. Found: C, 27.51; H,2.53.

1-Bromo-3,5,7-tris(acetylthiomethyl)adamantane (7). A solution of tritriflate **6** (0.212 g, 0.302 mmol), 18-crown-6 (1.12 g), and potassium thioacetate (0.384 g, 3.36 mmol) in acetonitrile (25 mL) was stirred at room temperature for 2 h. The resulting precipitate was removed by filtration, and the filtrate washed with

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[37] The roughness factor of the surface of our Au substrate was estimated to be at most 1.05 from the underpotential deposition of Pb^{2+}. For the method, see: Wong, S.-S.; Porter, M. D. *J. Electroanal. Chem.* **2000**, *485*, 135.

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5% NaCl and dried ($MgSO_4$). Evaporation of the solvent followed by separation by GPC (JAIGEL 1H+2H, $CHCl_3$) afforded **7** (0.116 g, 80%) as colorless crystals: mp 110−111 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (d, $J = 12.2$ Hz, 3H), 1.28 (d, $J = 12.2$ Hz, 3H), 1.95 (s, 6H), 2.37 (s, 9H), 2.80 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 30.7, 38.6, 40.0, 42.7, 50.7, 62.3, 194.9. Anal. Calcd for $C_{19}H_{27}BrO_3S_3$: C, 47.59; H, 5.68. Found: C, 47.87; H, 5.71.

1-Bromo-3,5,7-tris(mercaptomethyl)adamantane (1). A solution of potassium hydroxide (0.26 g) in methanol (10 mL) was added to **7** (42.8 mg, 0.089 mmol) in methanol (30 mL). The mixture was stirred at 0 °C for 1 h and acidified with 10% HCl (3 mL). The solvent was evaporated and the residue extracted with 20 mL of ethyl acetate. Evaporation of the solvent and subsequent recrystallization from chloroform gave 17.3 mg (55%) of **1** as colorless crystals: mp 107−108 °C; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, $J = 9.0$ Hz, 3H), 1.27 (d, $J = 12.0$ Hz, 3H), 1.36 (d, $J = 12.0$ Hz, 3H), 2.03 (s, 6H), 2.44 (d, $J = 9.0$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 36.6, 39.0, 42.3, 51.0, 63.5. Anal. Calcd for $C_{13}H_{21}BrS_3$: C, 44.18; H, 5.99. Found: C, 44.44; H, 5.94.

1-(4-Bromophenyl)-3,5,7-tris[(trifluoromethylsulfonyloxy)methyl]adamantane (8). To a solution of tritriflate **6** (0.374 g, 0.533 mmol) in CH_2Cl_2 (60 mL) and bromobenzene (6 mL) was added $AgSbF_6$ (0.699 g, 2.03 mmol). The mixture was refluxed for 7 h and washed with 5% $NaHCO_3$ and water. The solvent was evaporated under reduced pressure, and the residue was purified by GPC (JAIGEL 1H+2H, $CHCl_3$) to give 0.293 g (71%) of **8** as colorless crystals: mp 129−130 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6H), 1.74 (s, 6H), 4.27 (s, 6H), 7.18 (d, $J = 8.7$ Hz, 2H), 7.50 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 35.8, 37.0, 37.9, 42.3, 83.1, 118.6 (q, $^1J_{CF} = 320$ Hz), 121.0, 126.4, 131.9, 145.1. Anal. Calcd for $C_{22}H_{22}BrF_9O_9S_3$: C, 33.99; H, 2.85. Found: C, 33.90; H, 2.89.

1-(4-Bromophenyl)-3,5,7-tris(acetylthiomethyl)adamantane (9). A solution of tritriflate **8** (0.177 g, 0.228 mmol), 18-crown-6 (0.716 g), and potassium thioacetate (0.260 g, 2.28 mmol) in acetonitrile (25 mL) was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure and the residue dissolved in ethyl ether. The solution was washed with 5% NaCl and water, dried ($MgSO_4$), and evaporated. Purification of the residue by MPLC (SiO_2, hexane−ether 3:1) afforded **9** (99.6 mg, 79%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6H), 1.49 (s, 6H), 2.36 (s, 9H), 2.84 (s, 6H), 7.16 (d, $J = 8.7$ Hz, 2H), 7.42 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.7, 35.8, 38.1, 40.9, 43.6, 45.3, 119.9, 126.8, 131.3, 147.5, 195.3. Anal. Calcd for $C_{25}H_{31}BrO_3S_3$: C, 54.04; H, 5.62. Found: C, 54.34; H, 5.58.

1-(4-Bromophenyl)-3,5,7-tris(mercaptomethyl)adamantane (2). A solution of potassium hydroxide (0.16 g) in methanol (10 mL) was added to a solution of **9** (28.1 mg, 0.051 mmol) in methanol−ethyl ether (4:1, 12 mL), and the mixture was stirred at room temperature for 1 h. The mixture was acidified with 10% HCl (1.5 mL) and evaporated under reduced pressure. The residue was dissolved in CS_2 and quickly passed through a short column of SiO_2 to give **2** (17.1 mg, 79%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, $J = 9.0$ Hz, 3H), 1.31 (s, 6H), 1.56 (s, 6H), 2.48 (d, $J = 9.0$ Hz, 6H), 7.24 (d, $J = 9.0$ Hz, 2H), 7.44 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 35.9, 37.4, 38.3, 43.1, 45.4, 119.9, 126.9, 131.3, 147.9; HRMS (EI+) *m/z* calcd for $C_{19}H_{25}BrS_3$ (M^+) 428.0302, found 428.0307.

1-Phenyl-3,5,7-tris[(trifluoromethylsulfonyloxy)methyl]adamantane (10). To a solution of tritriflate **6** (0.213 g, 0.304 mmol) in CH_2Cl_2 (35 mL) and benzene (4 mL) was added $AgSbF_6$ (0.522 g 1.52 mmol). The mixture was refluxed for 90 h and then washed with 5% $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated. Purification of the residue by GPC (JAIGEL 1H+2H, $CHCl_3$) afforded **10** (0.177 g, 83%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 6H), 1.76 (s, 6H), 4.27 (s, 6H), 7.24−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 35.8, 37.0, 37.8, 42.4, 83.4, 118.6 (q, $^1J_{CF} = 320$ Hz), 124.5, 127.0, 128.7, 146.1; HRMS (EI+) *m/z* calcd for $C_{22}H_{23}F_9O_9S_3$ (M^+) 698.0360, found 698.0355.

1-(4-Iodophenyl)-3,5,7-tris[(trifluoromethylsulfonyloxy)methyl]adamantane (11). A solution of **10** (0.273 g, 0.391 mmol), $C_6H_5I(OCOCF_3)_2$ (0.194 g, 0.451 mmol), I_2 (98.9 mg, 0.390 mmol) in CCl_4 (1.3 mL) was stirred for 4 h at room temperature. The mixture was diluted with chloroform (30 mL), washed with 5% $NaHSO_3$ and 10% NaCl, and dried ($MgSO_4$). Evaporation of the solvent followed by GPC separation (JAIGEL 1H+2H, $CHCl_3$) afforded a colorless solid (0.272 g) consisting of **11** and byproduct **12** in a 4:1 ratio. The solid was recrystallized from chloroform to yield 0.179 g (56%) of pure **11**. The mother liquor was concentrated and chromatographed (SiO_2, hexane−ether 2:1) to give 27.4 mg (7.4%) of **12**.

11: colorless crystals; mp 147−148 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6H), 1.73 (s, 6H), 4.26 (s, 6H), 7.05 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 35.8, 37.0, 37.9, 42.3, 83.1, 92.5, 118.6 (q, $^1J_{CF} = 320$ Hz), 126.6, 137.8, 145.8; HRMS (FAB+) *m/z* calcd for $C_{22}H_{22}F_9IO_9S_3$ (M^+) 823.9327, found 823.9327.

12: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6H), 1.71 (s, 6H), 4.27 (s, 6H), 7.00 (dd, $J = 8.1$, 2.1 Hz, 1H), 7.75 (d, $J = 2.1$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 35.8, 36.9, 37.7, 42.1, 83.0, 106.1, 108.8, 118.6 (q, $^1J_{CF} = 320$ Hz), 125.8, 135.9, 139.5, 147.8; HRMS (FAB+) *m/z* calcd for $C_{22}H_{21}F_9I_2O_9S_3$ (M^+) 949.8293, found 949.8302.

1-(4-Iodophenyl)-3,5,7-tris(acetylthiomethyl)adamantane (13). A solution of tritriflate **11** (70.0 mg, 0.085 mmol), 18-crown-6 (0.340 g), and potassium thioacetate (0.110 g, 0.96 mmol) in acetonitrile (17 mL) was stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure and the residue dissolved in ethyl ether. The solution was washed with 5% NaCl, dried ($MgSO_4$), and evaporated. Purification of the residue by GPC (JAIGEL 1H+2H, $CHCl_3$) afforded **13** (45.9 mg, 90%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 6H), 1.48 (s, 6H), 2.36 (s, 9H), 2.84 (s, 6H), 7.04 (d, $J = 8.6$ Hz, 2H), 7.62 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.7, 35.8, 38.2, 40.9, 43.6, 45.2, 91.4, 127.1, 137.3, 148.2, 195.2; HRMS (FAB+) *m/z* calcd for $C_{25}H_{31}IO_3S_3$ ($M + H^+$) 603.0558, found 603.0554.

1-(4-Iodophenyl)-3,5,7-tris(mercaptomethyl)adamantane (3). A solution of potassium hydroxide (0.26 g) in methanol (15 mL) was added to **13** (24.8 mg, 0.041 mmol) in methanol−ethyl ether (3:1, 13 mL), and the mixture was stirred at room temperature for 1 h. The mixture was acidified with 10% HCl (2 mL) and evaporated under reduced pressure. The residue was extracted with ethyl ether (20 mL), and the ethyl ether was evaporated to give **3** (16.8 mg, 86%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, $J = 9.0$ Hz, 3H), 1.30 (s, 6H), 1.55 (s, 6H), 2.47 (d, $J = 9.0$ Hz, 6H), 7.11 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 35.9, 37.4, 38.4, 43.1, 45.3, 91.4, 127.2, 137.3, 148.6; HRMS (EI+) *m/z* calcd for $C_{19}H_{25}IS_3$ (M^+) 476.0163, found 476.0157.

1-[(Trifluoromethylsulfonyloxy)methyl]adamantane (1-AdCH$_2$-OTf). A solution of trifluoromethanesulfonic anhydride (0.84 g, 3.0 mmol) in CH_2Cl_2 (8 mL) was added dropwise to a solution of 1-(hydroxymethyl)adamantane (0.262 g, 1.58 mmol) and pyridine (1.0 mL) in CH_2Cl_2 (9 mL) with stirring at 0 °C over a period of 15 min, and the reaction mixture was stirred at 0 °C for 2 h. The mixture was diluted with CH_2Cl_2 (30 mL), washed with 10% HCl and 5% $NaHCO_3$, and dried ($MgSO_4$). The solvent was removed under reduced pressure to give essentially pure 1-AdCH$_2$OTf (0.454 g, 96%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.58 (d, $J = 2.4$ Hz, 6H), 1.65 (d, $J = 12.5$ Hz, 3H), 1.76 (d, $J = 12.5$ Hz, 3H), 2.04 (br. s, 3H), 4.08 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 27.6, 33.8, 36.5, 38.2, 86.3, 118.6 (q, $^1J_{CF} = 319$ Hz). Anal. Calcd for $C_{12}H_{17}F_3O_3S$: C, 48.31; H, 5.74. Found: C, 47.97; H, 5.87.

1-(Acetylthiomethyl)adamantane (1-AdCH$_2$SAc). A solution of 1-AdCH$_2$OTf (0.252 g, 0.845 mmol), 18-crown-6 (0.766 g), and potassium thioacetate (0.302 g, 2.64 mmol) in acetonitrile (30 mL) was stirred at room temperature for 2 h. The acetonitrile was evaporated, and the residue was dissolved in 30 mL of ethyl ether. The ether solution was washed with 5% NaCl and dried ($MgSO_4$). Evaporation of the solvent gave a brown oil, which was passed through a short column of SiO_2 and separated by GPC (JAIGEL 1H+2H, $CHCl_3$) to afford 1-$AdCH_2SAc$ (0.101 g, 53%) as colorless crystals: mp 30−31 °C; ^1H NMR ($CDCl_3$) δ 1.50 (d, $J = 2.7$ Hz, 6H), 1.60 (d, $J = 12.2$ Hz, 3H), 1.69 (d, $J = 12.2$ Hz, 3H), 1.96 (s, 3H), 2.35 (s, 3H), 2.73 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 28.4, 30.7, 33.2, 36.7, 41.3, 42.4, 196.0. Anal. Calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98. Found: C, 69.59; H, 9.07.

1-(Mercaptomethyl)adamantane (15). A solution of potassium hydroxide (0.58 g) in methanol (15 mL) was added to 1-$AdCH_2$-SAc (0.101 g, 0.450 mmol) in methanol (15 mL), and the mixture was stirred at room temperature for 1 h. The methanol was evaporated, and the residue was dissolved in 20 mL of ethyl ether. The ether solution was washed with 10% HCl and 5% $NaHCO_3$ and dried ($MgSO_4$). The solvent was removed under reduced pressure to give **15** (70.9 mg, 86%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.10 (t, $J = 8.6$ Hz, 1H), 1.52 (d, $J = 2.4$ Hz, 6H), 1.62 (d, $J = 12.0$ Hz, 3H), 1.71 (d, $J = 12.0$ Hz, 3H), 1.99 (br. s, 3H), 2.30 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.5, 33.1, 36.9, 38.7, 41.0; HRMS (EI+) m/z calcd for $C_{11}H_{18}S$ (M^+) 182.1129, found 182.1132.

X-ray Structural Analysis. Single crystals of **1** were obtained by recrystallization from chloroform. Intensity data were collected at 100 K on a Bruker SMART APEX diffractomater with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions: $C_{13}H_{21}BrS_3$; FW = 353.39, crystal size 0.40 × 0.40 × 0.30 mm^3, monoclinic, $P2(1)/n$, $a = 9.5204(6)$ Å, $b = 10.3261(7)$ Å, $c = 15.3043(10)$ Å, $\beta = 101.7830(10)°$, $V = 1472.84(17)$ Å^3, $Z = 4$, $D_c = 1.594$ g cm^{-3}. The refinement converged to $R_1 = 0.0270$, w$R_2 = 0.0738$ ($I > 2\sigma(I)$), GOF = 1.001.

Preparation of Self-Assembled Monolayers on Au(111). Gold substrates were prepared by the method reported previously.[33,34,42] Gold (99.99%) was vapor-deposited on freshly cleaved mica sheets at a reduced pressure, $<10^{-3}$ Pa. The mica was baked at 580 °C for 6 h prior to the deposition of the gold and this temperature was maintained during the deposition. The typical evaporation rate and thickness of the gold films were 1.0−1.5 nm/s and 200 ± 5 nm, respectively. The Au-deposited mica sheets were cut into 2 cm × 2 cm (for cyclic voltammetry) or 1 cm × 2 cm (for STM analysis) pieces, annealed at 530 °C for 8 h, and then quenched in Millipore purified water (resistivity >18 MΩ·cm, Millipore Simplicity 185 Water System). STM analysis of the gold film prepared in this way confirmed the formation of large Au(111) terraces.

For the preparation of the SAMs of **1** and **2**, the substrate was washed with EtOH and immersed in a 0.1 mmol/L solution of the thiol. For the preparation of the SAMs of **3**, which is not well soluble in EtOH, the substrate was washed with CH_2Cl_2 after washing with EtOH, and then immersed in a 0.1 mmol/L solution of **3** in CH_2Cl_2. In both cases, the substrates were kept immersed at room temperature in the dark for 24 h, rinsed with pure EtOH or CH_2Cl_2 and dried in air.

Polarization Modulation-Infrared Reflection Absorption Spectroscopy. PM-IRRAS spectra were recorded with a Thermo-Mattson Infinity spectrometer equipped with a HgCdTe detector cooled with liquid N_2 and a photoelastic modulator (Hinds, PEM-90) with the optical layout similar to that reported in the literature.[43] The signal was demodulated with a synchronous sampling demodulator (GWC Instruments). The spectra were collected over 10000 scans at a resolution of 4 cm^{-1}. More precisely, one cycle of recording, which consists of 10 consecutive scans for baseline, 100 scans for sample, 100 scans for sample, and 10 scans for baseline, was repeated 50 times. It took about 4 h for each sample. The differential reflectance was numerically converted to absorbance. All measurements were made in the air at room temperature.

Scanning Tunneling Microscopy. STM images were recorded under 0.1 M aq. $HClO_4$ using a Pico-SPM (Molecular Imaging Co.) and NanoScope III controller (Digital Instruments Inc.). An electrochemical system composed of a Pt wire counter electrode and a Ag wire reference electrode was used. Measurements were performed in the constant current mode using $Pt_{0.8}Ir_{0.2}$ tips coated with Apiezon wax.

Cyclic Voltammetry. Cyclic voltammograms of the reductive desorption were recorded in 0.5 mol/L KOH using a Ag/AgCl/sat. KCl electrode as the reference electrode and a platinum wire as the counter electrode. The gold substrate was mounted at the bottom of a cone-shaped cell using an O-ring and a clamp. The exposed area of the working electrode was 0.152 cm^2 (2.2 mm diameter circle). The solution in the cell was deaerated by bubbling H_2O-saturated argon for 30 min. Voltammograms were recorded on a BAS 100B electrochemical analyzer.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of new compounds and crystallographic data (table and CIF) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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