Triptycene Tripods for the Formation of Highly Uniform and Densely Packed Self-Assembled Monolayers with Controlled Molecular Orientation

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ABSTRACT: When employing self-assembled monolayers (SAMs) for tuning surface and interface properties, organic molecules that enable strong binding to the substrate, large-area structural uniformity, precise alignment of functional groups, and control of their density are highly desirable. To achieve these goals, tripod systems bearing multiple bonding sites have been developed as an alternative to conventional monodentate systems. Bonding of all three sites has, however, hardly been achieved, with the consequence that structural uniformity and orientational order in tripod SAMs are usually quite poor. To overcome that problem, we designed 1,8,13-trimercaptomethyl-triptycene (T1) and 1,8,13-trimercaptoptriptycene (T2) as potential tripod SAM precursors and investigated their adsorption behavior on Au(111) combining several advanced experimental techniques and state-of-the-art theoretical simulations. Both SAMs adopt dense, nested hexagonal structures but differ in their adsorption configurations and structural uniformity. While the T2-based SAM exhibits a low degree of order and noticeable deviation from the desired tripodal anchoring, all three anchoring groups of T1 are equally bonded to the surface as thiolates, resulting in an almost upright orientation of the benzene rings and large-area structural uniformity. These superior properties are attributed to the effect of conformationally flexible methylene linkers at the anchoring groups, absent in the case of T2. Both SAMs display interesting electronic properties, and, bearing in mind that the triptycene framework can be functionalized by tail groups in various positions and with high degree of alignment, especially T1 appears as an ideal docking platform for complex and highly functional molecular films.

INTRODUCTION

Self-assembled monolayers (SAMs) enable tailoring the wettability, adhesiveness, and work-functions of solid substrates as well as organic/inorganic hybrid interfaces. As surfaces and interfaces typically determine the performance of devices especially at the nanoscale, the application of SAMs is of particular technological importance. Besides conventional monodentate SAMs with a single anchor group, several types of molecular platforms with multiple anchoring sites have recently been developed. This aims at more effectively controlling the orientation, spatial and lateral arrangement, and density of the molecules bonded to solid surfaces. Moreover, multiple anchoring groups help in achieving a robust anchoring configuration. Of particular interest in this context are molecular tripods that usually consist of rigid tetrahedral cores bearing three anchors, such as thiol groups for binding to Au(111). Examples for such systems include triarylmethane-based molecular tripods featuring an sp3-hybridized carbon core or silicon core in Figure 1a). Also, a methylene thiol-appended adamantane-based tripod (C in Figure 1a) has been reported to form a hierarchical chiral network structure on Au(111). Recently, Mayor et al. investigated the impact of the configuration of anchor groups on the surface adsorption behavior, by comparing triarylmethane-based molecular tripods with meta-
and para-type substitution patterns ($D_{mec}$ and $D_{para}$ in Figure 1a). They showed that the former can form covalently bonded monolayers on Au(111), while the latter only grow in the bridgehead position.29,30 There, the triptycene moieties based monolayers with a single thiol or selenol group attached triply substituted triptycenes should offer a well-controlled molecular density and orientation. Notably, starting point for the development of ideal SAMs featuring tripods (Figure 1b) bearing anchoring thiol groups attached to the 1,8,13-positions of the triptycene framework either directly ($T_1$) or via a methylene linker ($T_2$). Free rotation of the single bonds in $A$–$D$, highlighted by the curved red arrows, might result in anchoring groups pointing away from the substrate. In contrast, the three sulfur atoms of both $T_1$ and $T_2$ are arranged in a plane parallel to the triptycene independent of the conformation of the molecule, promoting three-point adsorption on a solid surface.

Figure 1. (a) Schematic structures of selected examples of reported molecular tripods (A–D). (b) Chemical structures of 1,8,13-substituted triptycene-based molecular tripods ($T_1$ and $T_2$). Free rotation of the single bonds in $A$–$D$, highlighted by the curved red arrows, might result in anchoring groups pointing away from the substrate. In contrast, the three sulfur atoms of both $T_1$ and $T_2$ are arranged in a plane parallel to the triptycene independent of the conformation of the molecule, promoting three-point adsorption on a solid surface.

between the sulfur atoms in $T_2$ quite closely fit the lattice structure of Au(111).31 $T_1$ possesses a certain conformational flexibility due to the possibility of C–C bond-rotation in the thiol-containing functionality (Figure 1b, curved red arrow). Such a rotation allows adjusting the distances between the docking atoms without changing the plane in which the sulfur atoms are arranged. It also does not change the bonding geometry relative to the substrate, which for $T_1$ is different from that in $T_2$ due to the different inclination of the sulfur–carbon bonds. Overall, both $T_1$ and $T_2$ are designed to promote three-point adsorption on a solid surface.

A general advantage of triptycenes as anchoring platforms is that they can be substituted with functional units in various ways taking advantage of the four vacant sites per molecule, that is, the bridgehead,25 4, 5, and 16-positions.24 To lay the foundations for the further development of triptycene-anchored SAMs, in the present study we focus on the self-assembly behavior of the fundamental triptycene-based tripods $T_1$ and $T_2$ on Au(111). For that, we use a variety of complementary experimental tools, including scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and Kelvin probe (KP). The experimental findings are rationalized through dispersion-corrected density functional theory (DFT) simulations. We demonstrate that the triptycene-based tripods, especially $T_1$, can adopt an adsorption configuration with (nearly) all thiol groups equivalently bonded to the substrate. Moreover, the $T_1$ molecules in the monolayers display an almost upright molecular orientation, an exceptionally high degree of order, and interesting electronic properties.

RESULTS AND DISCUSSION

Synthesis of $T_1$ and $T_2$. The synthesis of $T_1$ is illustrated in Scheme 1. The reaction of 1,8,13-trihydroxytriptycene (3) with trific anhydride ($T_F^3O$) in the presence of pyridine gave tristriazine 4,24 which was converted into 5 by a Kumada–Tamao coupling reaction23,25 using methylmagnesium chloride and Ni(ddpp)Cl$_2$ (ddpp = 1,3-bis(diphenylphosphino)-propane). Compound 5 was reacted with N-bromosuccinimide (NBS) in the presence of azobis(isobutyronitrile) (AIBN),33 affording 6. Treatment of 6 with potassium thiocetate (AcSK)35 gave 7, whose acetyl groups were hydrolyzed with HBr, which was generated in situ from acetyl bromide (AcBr) and MeOH,35 to afford 1,8,13-trimercaptomethyltriptycene $T_1$.38

| Scheme 1. Synthesis of $T_1$ |
|---|
| a | b |
| c | d | e |

Reagents and conditions: (a) $T_F^3O$, pyridine, 1,2-dichloroethane, 0–60 °C, 97%; (b) MeMgCl, Ni(ddpp)Cl$_2$, THF, 80 °C, 80%; (c) NBS, AIBN, benzene, 50 °C, 59%; (d) AcSK, THF, 25 °C, 79%; (e) AcBr, MeOH, THF, –78 to 25 °C, 88%.

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1,8,13-Trimercaptotriptycene T2 was synthesized from 3 according to Scheme 2. The hydroxyl groups of 3 were acylated with N,N-dimethylthiocarbamoyl chloride in the presence of NaH to give 8. Upon heating of 8 at 260 °C in diphenyl ether, the Newman–Kwart rearrangement occurred to afford 9. The carbamoyl groups of 9 were hydrolyzed with KOH in a mixture of MeOH and THF, resulting in T2. Compounds T1 and T2 were unambiguously characterized by ¹H and ¹³C NMR spectroscopy, by FT-IR spectroscopy, and by high-resolution APCI-TOF mass spectrometry (Figures S18–S22 and Figures S30–S33 for T1 and T2, respectively; see the Supporting Information). Successful preparation of single crystals of T1 suitable for X-ray analysis allowed us to further determine the molecular structure of T1 (Figure S1; see the Supporting Information).

**Preparation of SAMs of T1 and T2 on Au(111).** Standard thermally evaporated Au(111) substrates were used. SAMs of T1 (T1/Au) and T2 (T2/Au) were fabricated by simply immersing Au(111) substrates into a degassed THF solution of T1 and T2 for 24 h at 25 °C. The samples then were washed with THF, dried under ambient conditions, and annealed at 120 °C. Further details are provided in the Experimental Section. As a reference sample for the spectroscopic analysis, we also prepared benzythiol (B1) SAMs on Au(111) using a standard procedure.

**STM Imaging of T1/Au and T2/Au SAMs.** Large-area (50 nm × 50 nm) STM images of T1/Au (Figure 2a) and T2/Au (Figure 2b) both show smooth and homogeneous terraces with steps of ca. 2.5 Å, which is consistent with the well-known interlayer spacing at Au terraces on the surface of Au(111). This observation suggests that T1 and T2 cover the Au(111) surface uniformly. Close-up views (10 nm × 10 nm) of T1/Au (Figure 2c) and T2/Au (Figure 2d), which focus on a terrace, are very similar to one another and display hexagonally aligned bright spots at ca. 5 Å separation, indicating that both T1 and T2 self-assemble on Au(111) to form highly ordered domains. We assume that the bright spots stem from the phenyl rings of the triptycene units (as their most conductive parts directly contribute to the Au bonding state, packing density, orientation, and configuration of the triptycene molecules. Figure 3 shows representative S 2p (Figure 3a–c) and C 1s (Figure 3d–f) XP spectra of T1/Au and T2/Au, along with those of B1/Au as a reference. The S 2p spectrum of T1/Au (Figure 3a) is very similar to that of B1/Au (Figure 3c): It is dominated by a characteristic S 2p doublet of thiolate bound to Au (Figure 3a, doublet 1) at ~162.0 eV (S 2p3/2), with an only small (~10%) admixture of an additional feature at 161.0 eV (S 2p1/2).38 This suggests that almost all “legs” of the triptycene molecules in T1/Au are bound to the Au substrate as thiolates. This is an exceptionally good result for tripod-type molecules, which usually exhibit multiple bonding geometries with a significant portion of unbound and weakly bound anchoring groups.5,39,40

The small feature at 161.0 eV (Figure 3a, doublet 2) is frequently observed in high-resolution XP spectra of thiolate-based SAMs and is also present in the reference B1/Au SAM (Figure 3c). It can be attributed either to an anchoring configuration differing from a thiolate or, more likely, to atomic sulfur bound to the substrate, as discussed in detail in ref. 38. Note that a small amount of atomically bound sulfur should not disturb the molecular packing, as the thiolate groups are quite loosely packed on the surface (see below).

The S 2p spectrum of T2/Au is also dominated by a characteristic S 2p doublet of thiolate bound to Au (Figure 3b, doublet 1). However, this spectrum contains noticeable contributions associated with physiosorbed/unbound thiols (Figure 3b, doublet 3; ~163.4 for S 2p3/2) and oxidized thiol groups (Figure 3b, doublet 4; ~167.5 for S 2p1/2). The latter feature corresponds to sulfonate, which is the most commonly
observed oxidized species in thiolate SAMs,1,38,41–43 that bonds only weakly to the substrate. For the spectrum presented in Figure 3b, the portions of the physisorbed/unbound thiols and sulfonate sulfur were estimated to be \( \pm 1.5\text{Å} \) for the thickness, \( \pm 10\% \) for the packing density, and \( \pm 3\% \) for the average tilt angle.4 In the simulations, work-function changes are reported relative to a calculated work-function of a relaxed Au surface of 5.13 eV. The slightly smaller value of the simulated packing density is a consequence of using the calculated Au lattice constants for reasons discussed in the Experimental Section.

Figure 3. (a–c) S 2p and (d–f) C 1s XP spectra of T1/Au (a,d), T2/Au (b,e), and B1/Au (c,f) SAMs. Individual doublets in the S 2p spectra are color-coded and marked by numbers (see text for details); background is shown by gray dashed line.

Table 1. Observed and Calculated Effective Thickness, Packing Density of the Thiolate Groups, Average Molecular Tilt Angle of the \( \pi \) Plane (\( \alpha \)), Average Molecular Tilt Angle of the \( \pi \) Plane (\( \beta \)), Work-Function Changes (\( \Delta \Phi \)), and Position of the Calculated XPS Peaks (Binding Energy) of T1/Au, T2/Au, and B1/Au

| system   | effective thickness (Å) | packing density/10\(^{14}\) (thiolate/cm\(^2\)) | average tilt angle of \( \pi \) plane \( \alpha \) (deg) | average molecular tilt angle \( \beta \) (deg) | work-function change \( \Delta \Phi \) (eV) | binding energy (eV) |
|----------|-------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|----------------------|
| T1/Au    | 9                       | 4.6                                           | 4.6                                           | 67                                            | 7.5                                           | 10.3                 |
|          |                         | XPS                                           | calc\(^d\)                                     | NEXAFS                                         | calc\(^d\)                                     | XPS MBQD            |
|          |                         | 81                                            | 86.8                                          | 36                                            | 3.4                                           | 14.0                |
| T2/Au    | 10.5                    | 4.6                                           | 4.1                                           | 67                                            | 85.1                                          | 14.0                |
|          |                         | XPS                                           | calc\(^d\)                                     | NEXAFS                                         | calc\(^d\)                                     | XPS MBQD            |
|          |                         | 67                                            | 85.1                                          | 80                                            | 77.4                                          | 14.0                |
| B1/Au    | 7                       | 3.7                                           | 4.5                                           | 80                                            | 77.4                                          | 14.0                |
|          |                         | XPS                                           | calc\(^d\)                                     | NEXAFS                                         | calc\(^d\)                                     | XPS MBQD            |
|          |                         | 80                                            | 77.4                                          | 10                                            | 14.0                                          | 14.0                |

"The tilt angle refers to the orientation of the phenyl rings with respect to the substrate normal. See text for details. The experimental errors are \( \pm 1.5\text{Å} \) for the thickness, \( \pm 10\% \) for the packing density, and \( \pm 3\% \) for the average tilt angle.4 In the simulations, work-function changes are reported relative to a calculated work-function of a relaxed Au surface of 5.13 eV. The slightly smaller value of the simulated packing density is a consequence of using the calculated Au lattice constants for reasons discussed in the Experimental Section.

The C 1s XP spectra of T1/Au (Figure 3d), T2/Au (Figure 3e), and B1/Au (Figure 3f) exhibit only one peak at 284.1, 284.5, and 284.1 eV, respectively. No contributions related to contaminations or oxidized species are observed, except for the spectrum of T1/Au, in which a very weak signal (asterisk) at \( \sim 286.5\text{eV} \) probably due to CO is perceptible. While the peak in the spectrum of B1/Au is symmetric, the C 1s peaks for T1/Au and T2/Au display some asymmetry, with a higher intensity at the low binding-energy side for T1/Au and the opposite situation for T2/Au.

A quantitative analysis of the XP spectra (for details, see the Experimental Section) provides information on the effective thickness of the SAMs and the packing density of the thiolate groups. The results are listed in Table 1. The packing density of the thiolate groups determined by the XPS analysis of T1/Au (\( 4.6 \times 10^{14}\) thiolate/cm\(^2\))\(^{45}\) agrees perfectly with the estimate from the STM imaging. It corresponds to the ideal value of ca. one S atom per \( \sqrt{3} \times \sqrt{3} \) surface unit cell and is also found for high-quality alkanethiolate SAMs on Au(111).\(^3\) This testifies to the ideal surface coverage in the T1/Au system. For T2/Au, the average coverage derived from the XPS data (\( 4.1 \times 10^{14}\) thiolate/cm\(^2\)) is somewhat smaller. The area-averaging character of the XPS measurements, in combination with the higher local coverage observed for T2/Au in the STM images, suggest the coexistence of densely packed and more defective (i.e., less densely packed) areas in T2/Au. Notably, all determined packing densities for the triptycene-based SAMs are distinctly higher than that of the reference B1 system (\( 3.7 \times 10^{14}\) thiolate/cm\(^2\)), underlining their superior quality. Consistently, the effective thickness of T1/Au is slightly higher than that of the reference B1/Au SAM (Table 1). The even higher effective thickness of T2/Au, despite the lower density of thiolate groups, is attributed to the presence of some physisorbed molecules.

NEXAFS spectroscopy experiments provided further insight into the structural quality of the SAMs and the molecular orientation. Representative data in Figure 4 comprise spectra acquired at the so-called magic angle of X-ray incidence (55°). They are independent of the molecular orientation and, thus, exclusively display the electronic structure of the SAMs.\(^{46}\) Additionally, the differences between the spectra acquired under normal (90°) and grazing (20°) incidence are shown. They provide information on the molecular orientation.\(^{40}\)

The SS\(^2\) spectra of T1/Au (Figure 4a) and T2/Au (Figure 4c) are similar to one another and also do not significantly deviate from the spectrum of B1/Au (Figure 4e) and from reported spectra of oligophenyl SAMs in general.\(^{47}\) They are dominated by the intensity \( \pi^* \) resonance of phenyl rings (Figure 4a, peak 1), which, however, appears at a slightly higher photon energy (\( \sim 285.3\text{eV} \)) than for benzene (\( \sim 285.0\text{eV} \))\(^{48}\) or oligophenyl SAMs (285.0–285.1 eV)\(^ {49}\) or even for triptycene SAMs with monodentate bonding configuration (\( \sim 285\text{eV} \)).\(^{50}\) We attribute that shift to a destabilization of the lowest unoccupied orbital in the triptycenes due to minor distortions of the phenyl rings by the central bridge, but, obviously, the tridentate bonding configuration is of importance as well. Additional low intensity resonances of oligophenyl SAMs, such as the R\(^*\)/C–S\(^*\) resonance at \( \sim 287.3\text{eV} \) and the \( \pi^* \) resonance at 288.8–288.9 eV (Figure 4c, peak 2), are also resolved in spectra.\(^{47}\) They are marginally smeared out for T1/Au and T2/Au, presumably due to their overlap with the features stemming from the sp\(^3\) carbons at the

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downward orientation of the anchoring groups, allowing upright molecular orientation of the phenyl rings relative to the substrate, in full agreement with the conclusions from the XPS data. The π-vector-like orbital,46 using the average tilt angle of the benzene blades of T1/Au (Figure 4a, peaks 3 and 4) at higher excitation energies. The 90°–20° NEXAFS spectra of T1/Au, T2/Au, and B1/Au exhibit pronounced linear dichroism (Figure 4b,d,f) with the effect being particularly strong for the πi* resonances of the phenyl rings (Figure 4a, peak 1). In view of the specific orientation of the respective orbitals (perpendicular to the ring plane), a positive sign of the πi* difference peaks suggests upright molecular orientation of the phenyl rings relative to the substrate. This geometry corresponds to a predominantly downward orientation of the anchoring groups, allowing efficient anchoring of the triptycene tripods to the substrate, in full agreement with the conclusions from the XPS data.

A quantitative analysis of the NEXAFS data was performed within the commonly applied theoretical framework,40 relying on the most prominent πi* resonance. To that aim, we correlated the dependence of its intensity on the incidence angle of the X-ray beams (θ) with a theoretical expression for a vector-like orbital,16 using the average tilt angle of the πi* orbitals (α)49 as the sole fitting parameter. The resulting values of α are 81°, 67°, and 80° for the T1/Au, T2/Au, and B1/Au, respectively (Table 1). Because of the 3-fold symmetry of T1 and T2, the average value of the molecular tilt angle (β) can be directly obtained from the dependence of the intensity of the πi* resonance on cos² θ.50 The resulting values of β are shown in Table 1, along with the value for the B1/Au SAM. The latter can, however, only be considered as a lower limit of the average tilt angle in that system due to the lower molecular symmetry, which results in a dependence of the calculated value of β on the molecular twist (here set to 0° yielding the minimum value of β for a given α).50

The average value of β for T1/Au is quite small (∼7.5°), suggesting that the benzene blades of T1 are almost perpendicular to the substrate, which agrees well with the identical adsorption mode of all three anchoring groups (Table 1). The deviation from the fully parallel orientation could be explained by a possible corrugation of the specific anchoring sites of the three thiolate groups. This is, however, not supported by the simulations (see below). Therefore, we rather attribute it to a (small) number of defects, for example, at domain boundaries or step edges, and to the grain structure of the substrate within the macroscopically large area probed by NEXAFS spectroscopy.

For T2/Au, the average value of β is noticeably higher (Table 1), reflecting the lower quality of this monolayer as compared to T1/Au. This does not necessarily mean that T2/Au SAM contains no highly ordered areas of well-aligned molecules (see, e.g., STM experiments). These domains, however, must then coexist with areas of inhomogeneously bound and probably even physisorbed molecules with a strongly inclined or even stochastic orientation. This notion is consistent with the interpretation of the S 2p XP spectra and the derived coversages discussed above.

**Computational Studies on the Structures of T1/Au and T2/Au.** To gain atomistic insight into the properties of the T1/Au(111) and T2/Au(111) SAMs, we performed dispersion-corrected density-functional theory (DFT) calculations on periodic, infinitely extended interfaces. To be consistent with the experimental situation, we generated densely packed SAMs by choosing a 3 × 3 Au surface unit cell containing one molecule. This results in a hexagonal arrangement of triptycene molecules (Figure 5a,b) with a packing density of 4.45 × 10¹⁴ thiolate/cm² consistent with the experimental values.51 The length of the resulting surface unit-
cell vectors is 8.82 Å, which is somewhat larger than the unit-cell vector in the bulk assemblies of tripropyl tritylene, such as 1,8,13-tridodecyloxytritylene (8.1 Å). This difference arises from the fact that the dimensions of the surface unit cell are determined by the periodicity of the Au substrate, while the periodicity in the bulk reflects the optimum intrinsic distance for a hexagonal assembly of tritylene molecules. Consequently, one can expect some strain in the adsorbate layer, which might be one of the reasons for the structural imperfections found particularly for T2 (without flexible methyl linkers).

A screening of possible anchoring sites for the densely packed monolayers yields S atoms located on the bridge sites shifted toward fcc hollow positions in the case of T1/Au and S atoms at fcc-hollow sites in T2/Au (Figure 5a,b). This is consistent with the computational results for isolated adsorbed molecules on Au(111). The difference in anchoring sites is clearly visible in Figure 5c,d, where only the S atoms on the Au(111) surface are shown. The site in T1/Au corresponds to the ideal anchoring position typically found when simulating thiolate-bonded SAMs on Au(111) using a methodology similar to the present one. The occurrence of a supposedly less ideal anchoring site in T2/Au is attributed to the structural rigidity of T2. It enforces an unusual arrangement of the S–C bonds nearly perpendicular to the Au surface, with the actual values of the angles between the bonds and the surface normal varying between 0.7° and 3.4°. The unusual thiolate bonding geometry results in some distortions of the molecular structure of T2 upon adsorption, with the distance between neighboring S atoms increasing by 0.2 Å as compared to an isolated molecule. For T2/Au also the heights of the three docking groups vary quite significantly (between 0.61 and 1.03 Å relative to the topmost Au layer), while they are essentially the same (1.16 Å) for all S atoms in T1/Au (see Figure 5e and f).

Consistent with the less ideal bonding configuration of T2/Au, the binding energy per molecule (representative of breaking the bond between the substrate and the adsorbate) is significantly smaller than that for T1/Au (5.43 eV vs 7.16 eV). A similar trend is observed for the adsorption energy characteristic of bond formation (1.62 eV vs 2.67 eV).

Simulated structural parameters for the adsorbed molecules are summarized in Table 1. The tilt angle of the π* orbitals (α) and the molecular tilt angles (β) for T1/Au are 86.8° and 3.4°, respectively, which is in good agreement with the NEXAFS results (α = 81° and β = 7.5°). Conversely, the simulated values for well-ordered T2/Au (α = 85.1° and β = 6.7°) differ significantly from the NEXAFS values (α = 67° and β = 36°). As indicated earlier, we attribute that to the coexistence of ordered and disordered domains in T2/Au, with essentially upright-standing molecules (β = 7.5°) in the ordered regions separated by severely disordered structures in between (see discussion of S 2p XP spectra).

**Electronic Properties of the Interface.** Functionalization of metal surfaces with SAMs is useful for tailoring the electronic properties of metal substrates. Here, the tritylene-based SAM systems have a particularly high potential as surface modifier, because of the following: (i) They form dense and ordered monolayers with, in the case of T1, essentially upright-standing molecules. (ii) They can be efficiently chemically modified with various (polar) functional groups at the SAM–ambient interface at the 4,5,16−25 and bridgehead positions. To establish the basis for future applications, we here discuss experimental and theoretical investigations of the electronic properties of the “parent” interfaces T1/Au and T2/Au.

Kelvin-probe experiments on T1/Au and T2/Au yield work-functions (Φ) of 4.40 and 4.45 eV, respectively. With a Φ value of a bare, freshly sputtered Au(111) substrate of 5.20 eV, this result in work-function modifications (ΔΦ) of −0.80 eV (for T1) and −0.75 eV (for T2). These values are comparable to those obtained for biphenylthiolate monolayers on Au(111) (Φ = 4.35−4.42 eV).

As Kelvin probe is an area-averaging technique, the similarity in the final work-function of T1/Au and T2/Au might seem surprising considering the much higher degree of disorder in the T2/Au films. Disorder ought to result in much less ideally aligned dipoles and, consequently, a distinctly reduced work-function modification. As this is not observed, we conclude that for an ideally arranged T2/Au interface, much larger work-function changes than for T1/Au should be observed.

To test this hypothesis, we resorted to the simulations, which describe the situation of two perfectly ordered monolayers: The calculated work-function modification for T1/Au (ΔΦ = −1.33 eV) somewhat overestimates the experimental value. This is in line with what we typically observe for polar SAMs and can partly be attributed to the residual disorder in the experiments caused by step edges and grain boundaries. Additionally, the calculated molecular dipoles and bond dipoles are influenced by the employed computational methodology (see the Supporting Information).

In line with the value for T1/Au, we calculate a work-function change of −1.38 eV for the biphenylthiolate SAM. In sharp contrast to those two cases, for a perfectly ordered T2/Au interface a much larger value of ΔΦ = −1.73 eV is obtained, as expected on the basis of the arguments in the previous paragraph.

What remains to be explained is why the intrinsic work-function change for a T2/Au interface is by ca. 0.4 eV larger than that for T1/Au. To clarify that, we performed the following test: We modeled benzylthiolate (B1) and benzenethiolate (B2) SAMs, which differ only in the presence of a methyl linker between the phenyl and the thiolate in the former system. A full geometry optimization for both systems results in structures with the S atoms in bridge position shifted toward fcc-hollow sites (i.e., consistent with the situation for T1/Au). This yields a slightly larger work-function change of −1.44 eV for B2/Au as compared to −1.33 eV for B1/Au. When the S atom of the B2 molecule is fixed at the fcc-hollow position (i.e., the favorable position for T2), the ΔΦ value for B2/Au increased to −1.52 eV. When additionally fixing the position of the C atom bonded to the thiolate to the position it assumes in T2/Au, ΔΦ rises further to −1.65 eV. This shows that the difference in ΔΦ between T2/Au and T1/Au arises from the different hybridization states of the C atom bonded to the thiolate (sp2 vs sp3 hybridized) and, even more importantly, from differences in the C–S–Au bonding geometries.

A more local view of the electrostatics of the SAMs can be gained from an in-depth analysis of the XPS data. The calculated C 1s XP spectra of T1/Au and T2/Au at a photon energy of 350 eV are reported in Figure 6. The energies scale is shifted by 18.88 eV in both systems to align the experimental and calculated maxima for T1/Au. Fully consistent with the experiments, the positions of the peak maxima in the calculations differ by 0.4 eV between T1/Au (Figure 6a, 284.1 eV) and T2/Au (Figure 6b, 284.5 eV). The
magnitude of that difference is close to the shift in $\Delta \Phi$ between the simulated T1/Au and T2/Au interfaces. As shifts in the electrostatic energy directly impact core-level binding energies,62 this further supports the notion that for perfectly ordered SAMs the interfacial dipoles are larger in the T2/Au case. The reason why the electrostatic shift is resolved in the XPS experiments despite the disordered regions is that binding energies are impacted by the local electrostatic potential at the position of the excited atom such that variations of the electrostatic potential do not average out.63 Figure 6 also shows the energetic positions of the C 1s core levels of the individual C atoms in the SAMs, which allows a direct comparison between T1/Au and T2/Au on an atom by atom level. Obviously, beyond the global shift between the spectra, the differences in binding energies between T1/Au and T2/Au are small for electrons from equivalent C atoms, except for CB and C1 carbons (see insets in Figure 6a,b). This confirms the earlier conclusion that differences in electrostatic energies and work-functions in the two SAMs originate from the immediate anchoring region.

CONCLUSIONS

Combining experimental and computational studies, we have demonstrated that triptycene-based molecular tripods (T1 and T2) with thiol-containing functionalities at the 1,8,13-positions self-assemble into dense, uniform, and ordered monolayers on a metal surface with an upright orientation of the benzene planes. The key of the molecular design of T1 and T2 is that the three thiol groups are attached to a rigid triptycene framework in a way that they can efficiently bond to a surface, irrespective of possible conformational states. Moreover, 1,8,13-substituted triptycenes have a strong tendency to adopt nested 2D hexagonal structures, which promotes the self-assembly process.

The synthesis of T1 and T2 is achieved by sequential organic transformations from 1,8,13-trihydroxytriptycene in good overall yields. STM imaging of T1 and T2 assembled on Au(111) suggests the formation of uniform self-assembled monolayers (SAM) with an ordered 2D hexagonal arrangement of the triptycenes. On the basis of our XPS data, we conclude that (nearly) all of the S atoms of T1 bind to Au(111). This results in an upright orientation of the molecules, as confirmed by NEXAFS measurements and quantum-mechanical simulations with a measured (calculated) tilt angle of $7.5^\circ$ (3.4°). Conversely, the SAM of T2 may contain significant amounts of unbound or weakly bound thiol groups, which causes partial oxidation of the thiol functionality. The large average tilt angle of $36^\circ$ of T2 on Au(111) determined by NEXAFS spectroscopy in combination with the STM, XPS, and modeling results suggests the coexistence of well-ordered domains with essentially upright standing molecules and highly disordered regions. The lower structural quality of the T2/Au interface can be traced back to a less favorable bonding arrangement in the immediate interface region, which also results in lower binding energies. Interestingly, despite the significantly different degrees of order in the T1 and T2 SAMs, the changes in the area-averaged work-function caused by the SAMs are essentially the same for both interfaces (ca. −0.8 eV). On the basis of the simulations and the XPS experiments, this can be rationalized by a significantly larger change in the well-ordered regions of T2/Au caused mostly by the different bonding geometry, which is eventually diminished by smaller values for the disordered parts of the film.

The results presented in this study establish a new type of tripodal SAM, whose architecture is distinctly different from conventional monolayers of molecular tripods. The advantages of the triptycene system, particularly T1, are the reliable tripodal adsorption configuration, the efficient large-area uniform 2D self-assembly, and an almost ideal upright orientation of the benzene rings, projected to the attached functional groups. Importantly, the triptycene tripods can be readily decorated using the bridgehead25 or the 4,5,16-positions.24 As either one or three functional groups per tripod can then be substituted, their density and separation can readily be varied. Thus, the presented systems can serve as stable and conformationally rigid anchors, for example, for polar entities modifying sample work-functions, for recognition functionalities in combination with biomolecules, or for receptor groups in sensing applications. This makes them highly promising building blocks for applications in organic and molecular circuits, biomedical devices, optical and chemical sensors, solid catalyst, and many more.

EXPERIMENTAL SECTION

Materials. Unless otherwise stated, all commercial reagents were used as received. Benzylthiol (B1) and hexadecanethiol (HDT) were purchased from Sigma-Aldrich. Compound 3 was prepared according to previously reported procedures23 and unambiguously characterized by nuclear magnetic resonance (NMR) spectroscopy and atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectrometry. For long-term storage of T1 and T2, these compounds were stored under an argon or nitrogen atmosphere in the freezer to avoid oxidation of the thiol groups.

General. NMR spectroscopy measurements were carried out on a Bruker AVANCE-500 spectrometer (500 MHz for $^1$H and 125 MHz for $^{13}$C).
for $^{13}$C) or AVANCE-400 spectrometer (400 MHz for $^1$H and 100 MHz for $^{13}$C). Chemical shifts ($\delta$) are expressed relative to the resonances of the residual nondeuterated solvents for $^1$H [CDCl$_3$, $^1$H($\delta$) = 7.26 ppm; acetone-$d_6$, $^1$H($\delta$) = 2.05 ppm] and $^{13}$C [CDCl$_3$, $^{13}$C($\delta$) = 77.16 ppm; acetone-$d_6$, $^{13}$C($\delta$) = 29.8 and 206.3 ppm]. Absolute values of the coupling constants are given in Hertz ($Hz$), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (b) (see the Supporting Information). Infrared (IR) spectra were recorded at 25 °C on a JASCO FT/IR-6600ST Fourier-transform infrared spectrometer. High-resolution mass spectrometry measurements were carried out on a Bruker microTOF II mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) probe or an electroSpray ionization (ESI) probe.

**STM Measurements.** STM tips were mechanically cut from a tungsten wire (diameter 0.25 mm; Nilaco). Au(111) substrates, obtained by thermal evaporation of Au onto a freshly cleaved mica substrate, were flame-annealed and quenched in ethanol prior to use. Samples for STM imaging were prepared by immersing an Au(111) substrate into a degassed THF solution (2.0 µmol/L) of T1 or T2 for 24 h, and the resultant substrate was washed with THF, dried in air, and then thermally annealed (120 °C, 1 h) under reduced pressure. Constant current-mode STM imaging was carried out on a Nanoscope III STM system (Digital Instruments). All STM measurements were performed at 25 °C in air. The STM scanner was calibrated with an Au(111) substrate prior to the experiments. The observed STM contrast (apparent height) difference of 2.5 Å was consistent with the well-known interlayer separation at Au terraces on Au(111).

**Preparation of SAMs for the Spectroscopy and Kelvin Probe Measurements.** The SAMs for these experiments were prepared on commercial Au substrates (Georg Albert PVD, Siz, Germany). These substrates were prepared by thermal evaporation of 30 nm of Au (99.99% purity) onto a polished single-crystal silicon (111) orientation. The SAMs were prepared by immersion of Au(111) substrate in a degassed THF solution (1.1 mM) of T1 or T2 for 1 h under reduced pressure. The resulting Au films were polycrystalline, having a grain size of 20–50 nm and predominantly exhibiting a (111) orientation. The SAMs were prepared by immersion of a fresh substrate in a degassed THF solution (2 µm–1 mM) of T1 or T2 for 24 h at 25 °C. After immersion, the films were washed with THF and dried by blowing argon. Finally, some of the samples were annealed at 100 °C for 1 h either under inert gas atmosphere or under ultrahigh vacuum (UHV) conditions. Additional, several reference SAMs, that is, those of B1 and HDT on Au(111), were prepared using standard procedures. HDT/Au was used as a reference system for the XPS and work-function measurements (see below). B1 can be regarded as a partial structure of T1, making it a suitable monothiol reference. Because of the presence of the methane linker between the benzene ring and thiol group, a suitable monolayer can be expected, similar to the analogous nitrile-substituted system. At the same time, we refrained from studying benzenethiol as the monothiol reference to T2, as it has been shown to form SAMs of only limited quality when employing the standard immersion procedure. XPS and NEXAFS Spectroscopy Measurements. The XPS, NEXAFS spectroscopy, and work-function measurements were performed under UHV conditions (1.5 × 10$^{-7}$ mbar) at 25 °C. Laboratory XPS measurements were carried out with a MAXX200 (Leybold-Heraeus) spectrometer equipped with an Mg Kα X-ray source (200 W) and a hemispherical analyzer. The spectra were corrected for the spectrometer transmission, and the binding energy (BE) scale was referenced to the Au 4f$_{7/2}$ peak at 84.0 eV. The quality of the laboratory spectra in terms of statistics and energy resolution was inferior to the synchrotron data, they were mostly used to verify the film thickness and packing density.

Synchrotron-based XPS measurements were carried out at the bending magnet HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin, Germany. This beamline provides a moderate X-ray intensity helping to avoid X-ray damage during the spectra acquisition. The spectra were collected with a Sciensa R3000 electron energy analyzer in normal emission geometry. The photon energy (PE) was set to either 350 or 580 eV, depending on the BE range. The BE scale was referenced to the Au 4f$_{7/2}$ peak at 84.0 eV. The energy resolution was ∼0.3 eV at a PE of 350 eV and ∼0.5 at 580 eV. The XPS data were used to calculate the effective thickness and packing density of the SAMs, relying on the C 1s/Au 4f and 52p/Au 4f intensity ratio using standard procedures. For the thickness evaluation, a standard expression for the attenuation of the photoemission signal was assumed together with literature values for the attenuation lengths. The spectrometer-specific coefficients were determined with the help of the reference HDT SAM with a known thickness (18.9 ± 0.1 Å) and packing density (4.63 × 10$^{14}$ molecules/cm$^2$; $\sqrt{3} \times \sqrt{3}$ structure). NEXAFS spectroscopy measurements were performed at the same beamline. The spectra were collected at the C K-edge in the partial electron yield mode with a retarding voltage of −150 V. The polarization factor of the X-ray’s was estimated as −88%; the energy resolution was ∼0.30 eV. The incidence angle of the light was varied from 90° (normal incidence geometry; E-vector in surface plane) to 20° (grazing incidence geometry; E-vector near surface normal) in steps of 10°−20°, which is a standard approach enabling the determination of the molecular orientation from NEXAFS data. Raw spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. The PE scale was referenced to the pronounced π* resonance of highly oriented pyrolytic graphite at 285.38 eV.

**Kelvin Probe Measurements.** Work-function measurements were carried out using a UHV Kelvin Probe 2001 system (KP technology Ltd., UK). The pressure in the UHV chamber was ∼10$^{-9}$ mbar. As reference, we used HDT/Au with the work-function value set to 4.30 eV according to the literature. The latter value was additionally verified by referencing it to the work-function of freshly sputtered gold set to 5.20 eV. The accuracy of the WF values is ca. ±0.03 eV.

**Computational Methodology.** The calculations were performed using the FHI-aims code and employing the PBE functional in combination with the surface parametrization of the Tkatchenko–Scheffler dispersion correction. The latter were turned off between the bulk Au atoms. Periodic boundary conditions and the repeated slab approach including a vacuum region of at least 20 Å in the z direction were employed to represent the interface. To compensate for the electrostatic asymmetry of the slab, a self-consistently calculated dipole layer was inserted in the vacuum. To sample the reciprocal space, a nonorthogonal 6 × 6 × 1 Γ-centered k-point grid was used. The dimensions of the unit cells in the x and y directions were defined according to the calculated Au nearest neighbor distance (2.940 Å), to avoid spurious surface relaxations. The metal was modeled using 5 layers of Au, with the bottom 3 layers fixed at their bulk positions during the optimization. The presented results were obtained using the default FHI-aims “tight” basis set and setting the total energy criterion for the self-consistency cycle to 10$^{-6}$ eV. The optimizations were performed until the maximum residual force component per atom was below 0.01 eV/Å. For the initial screening of different docking sites, less accurate settings were adopted, using the default FHI-aims “light” basis set and stopping the optimization when the maximum residual force component per atom was below 0.05 eV/Å.

Binding energies, $E_{\text{bind}}$, are defined such that they reflect the energy needed to break the bond between the molecule and the substrate and to remove the molecules from the SAM:$E_{\text{bind}} = E_{\text{Trip/Au}} - E_{\text{Au}} - E_{\text{Trip}}$(1)

Here, $E_{\text{Trip/Au}}$ is the energy per unit cell of the SAM adsorbed to the surface, $E_{\text{Au}}$ is the energy of the optimized pristine Au slab, and $E_{\text{Trip}}$ is the energy of the optimized gas-phase molecular radical. Conversely, adsorption energies, $E_{\text{ad}}$, reflect the energetics of forming the monolayers and at the same time replacing the molecular S−H bonds by bonds to the Au surface. They are, thus, defined as

$E_{\text{ad}} = E_{\text{Trip/Au}} - E_{\text{Au}} - E_{\text{Trip/Au}} + 3/2E_{112}$(2)
$E_{\text{trip}}$ in this equation represents the energy of the optimized gas-phase triptycene molecule in which all S atoms are saturated with hydrogens, and $E_{\text{H2}}$ is the energy of an isolated H2 molecule.

The XP spectra were simulated within the initial state approach to avoid artifacts arising from a combination of periodic boundary conditions and explicit excitations in each unit cell.62 For obtaining the spectra, the 1s core level energies for every C atom were taken from the atom projected density of states output files. Subsequently, they were shifted considering the screening of the core hole by the metal substrate via an electrostatic charge model63,64 assuming a dielectric constant of the SAM of 3.9.65 To model the spectra, the individual resonances were broadened using Gaussian functions with a variance of 0.15 eV and an intensity scaled using an exponential attenuation function to account for the finite escape depth of the photoelectrons. Additionally, the energy scales for both interfaces were rigidly shifted by the same energy to align the calculated and measured positions of the C 1s peaks for T1/Au. This is inevitable, considering that when employing the initial state approach, Kohn–Sham orbital energies are calculated. For more details, see refs 61 and 62.

In the simulations of the benzylthiolate (B1) and benzenethiolate (B2) SAMs, two molecules per (3 $\times$ $\sqrt{3}$) rect unit cell in a herringbone arrangement were considered. For that cell, we chose an orthogonal 9 $\times$ 5 $\times$ 1 Γ-centered k-point grid. When placing the molecules at specific adsorption sites, only the positions of the S atoms were fixed. All of the other were relaxed. When also fixing the molecular tilt, this was achieved by only fixing the coordinates of the C atom directly bonded to S.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b00950.

Details of synthesis, NMR, IR, high-resolution MS spectra, single-crystal X-ray structural analysis, and computational details (PDF)

X-ray crystallographic data for T1 (CIF)

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Notes

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