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A Tetrapodal Diazatriptycene Enforces Orthogonal Orientation in Self-Assembled Monolayers

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ABSTRACT: Conformationally rigid multipodal molecules should control the orientation and packing density of functional head groups upon self-assembly on solid supports. Common tripods frequently fail in this regard, because of inhomogeneous bonding configuration and stochastic orientation. These issues are circumvented by a suitable tetrapodal diazatriptycene moiety, bearing four thiol-anchoring groups, as demonstrated in the present study. Such molecules form well defined self-assembled monolayers (SAMs) on Au(111) substrates, whereby the tetrapodal scaffold enforces a nearly upright orientation of the terminal head group with respect to the substrate even in case of 75% covalent attachment to the surface. Functionalization by condensation chemistry allows a large variety of functional head groups to be introduced to the tetrapod, paving the path towards advanced surface engineering and sensor fabrication.

Introduction

Self-assembled monolayers (SAMs) are unique supramolecular architectures characterized by a high degree of order. SAMs are also relevant for applications: Alongside their use in biotechnology,¹ they are commonly employed in organic electronics. For instance they can be exploited directly as active (semi)conductive materials in SAM field-effect transistors (SAMFETs),^{2,3} or as passivators on top of a gate dielectric, reducing leak current and charge trapping states,⁴ which is important for low operation voltages.⁵ Further improvement of device efficiency can be achieved by dipolar SAMs which allow to tune the work function (WF) of the electrode and modulate the charge injection barrier.^{6,7} To achieve a maximum work function shift (WFS), the molecular dipole has to be perpendicular to the surface.⁸⁻¹⁰ Additionally, spatial and lateral control of the SAM's functional group is crucial for many single-molecule devices such as molecular wires, switches, rotors, sensors or redox-active or photochromic moieties.¹¹⁻²¹

Multipods allow generally a reasonable control of molecular orientation.^{11,12,17,22-27} The perpendicular orientation of the terminal head group or functional moiety relative to the surface is dictated by the binding mode to a rigid scaffold, which, in turn is either

covalently linked to the substrate via multipodal anchoring groups²⁸ or physisorption, either on metals^{17,18,25,26,29-35} or on other surface types.^{28,36,37} Common multipods exhibit three anchoring groups and one head group, usually linked by a central, sp³-hybridized carbon or silicon atom (Figure 1a).^{22,26,31} Other common examples for rigid, space-demanding tripodal scaffolds include adamantanes (Figure 1b),^{12,24} tetraphenylmethanes (Figure 1c)^{11,25} and tetraphenylsilanes,^{38,39} some of which form closely packed SAMs. However, modular derivatization of some of these scaffolds is challenging. Most importantly, insufficient binding was reported for most tripodal architectures with up to 30 % of anchoring groups not bound to the substrate.^{26,31-34,40-42} This drawback limits spatial and lateral control of the functional unit and yields defects in the 2D-lattices of the SAMs. Among rigid scaffolds, thiol-substituted triptycenes have been used on gold surfaces.⁴³⁻⁴⁵ Recently, some of us have investigated 1,8,13-trimercaptomethyltriptycene with reliable tripodal absorption and dense molecular packing,²³ whose further chemical derivatization to introduce different functional groups is, however, not straightforward. In comparison to tripodal anchors, fewer tetrapods exist due to lack of structures resulting in well-defined spatial

configurations.²⁸ Examples include porphyrins,^{46–48} resorcin[4]arenes,⁴⁹ as well as fluorene⁵⁰ and carbazole-based⁵¹ tetrapods. While the former are not capable of hosting different head groups and are spacious, the functional groups of fluorene and carbazole-based tetrapods are significantly tilted due to the flexible nature of the scaffold, resulting in intermolecular interactions and less dense packing. Rigid triptycenes with four flexible alkylen-based anchors have been suggested as tetrapodal scaffolds but not investigated on-surface.⁵²

Figure 1. Structures of several representative multipods. Tridentate with a) a tetraalkylmethane (silane) b) an adamantane core or c) a tetraphenylmethane (silane) scaffold, and d) tetradentate approach based on diazatriptycenes presented in this work; HG = head group, ⚓ = anchoring group.

We have designed and synthesized a new tetrapodal, rigid thiol-functionalized

diazatriptycene (Figure 1d) that forms robust and stable SAMs on gold substrates - with a nearly upright orientation of the functional tail group *even at partial anchoring* of the docking group. As our diazatriptycenes are formed by simple condensation reactions, our tetrapod can be easily derivatized, e.g. to construct surface-anchored dipoles, receptors/sensors or molecular switches, all of which require a precise orientation and alignment.^{11,13} We herein focus our attention on *ortho*-phenylenediamine to give diazatriptycene (**DAT**) (see Scheme 2). We performed a multi-technique characterization of **DAT** to explore the physical and chemical properties of its SAM on a gold substrate. We chose acetyl protected thiols as anchoring groups, as sulfur is one of the strongest and best investigated anchoring moieties for SAMs on gold.^{53–56} The four thioacetates at the rigid dibenzobarrelelene subunit were deprotected *in situ* during SAM formation; the free thiols chemisorb to the gold and enforce orthogonal orientation of the quinoxaline moiety with respect to the substrate.

Results and Discussion

Synthesis

The synthesis of the **DAT** SAM precursor is portrayed in Scheme 1. **Error! Reference**

source not found.. **DAT** was synthesized starting from **1**, available on a 100 g scale from veratrole and acetaldehyde,⁴⁸ and subjected to a Diels-Alder reaction with vinylene carbonate at 180°C furnishing **2** in 77 % yield. Hydrolysis of **2** with sodium hydroxide gave pinacol **3** (85 %), which was Swern-oxidized into the diketeto-derivative **4** on a multi-gram scale, a versatile building block for derivatization with amines, especially 1,2-diamines.^{57–60}

4 reacted with *o*-phenylenediamine to give **5** in 96 % yield; demethylation with BBr₃ furnishes **6** (71 %). Fourfold esterification with trifluoromethylsulfonic acid anhydride (Tf₂O) yielded the tetratriflate **7** in a yield of 29 % (73 % per functional group). As phenyl thiols are prone to oxidation, we installed the thioacetates in a two-step sequence. First, **7** underwent fourfold palladium-catalyzed cross-coupling with *tert*-butylmercaptane (94 %). Second, cleavage of the *tert*-butyl groups with AlCl₃ in toluene gave the free tetrathiol, used without further purification for the acylation employing triethylamine (TEA) and acetyl chloride (AcCl). The pale-yellow SAM precursor **DAT** was obtained in 37 % yield on a 100 mg scale over 2 steps and in an overall yield of 4 % starting from **1**. Note that although the methyl groups at the bridge head positions of **DAT** may slightly influence

packing of the SAM, they would not impact its binding geometry and orientation.

Scheme 1: Synthesis of the diketodibenzobarrelene building block **4** and the target compound **DAT**. (i) Vinylene carbonate, 1,2-dichlorobenzene, 180 °C, 5 d; (ii) Sodium hydroxide, 1,4-dioxane, reflux, 2 h; (iii) DMSO, TEA, TFFA, DCM, -78 °C, 3 h; (iv) *o*-phenylenediamine, DCM/HOAc, 90 °C, 3 h; (v) BBr₃, DCM, -78 °C, 1 d; (vi) TEA, Tf₂O, DCM, -78 °C, 2 h; (vii) [Pd], *tert*-butylthiol, THF, 100 °C, 5 d (viii) AlCl₃, TEA, acetyl chloride, toluene, rt, 16 h.

SAM Formation

SAMs were prepared by a standard immersion procedure: To a 0.025 mM **DAT** solution in THF/methanol 1/3 (3 mL) were added polycrystalline gold substrates and 1 M methanolic solution of ammonia as a cleaving agent (1 mL), resulting in an overall concentration of **DAT** of 0.015 mM. After immersion for 10 min, samples were rinsed with MeOH, sonicated in MeOH and THF for 10 min and dried (details see SI, section 4).^{25,61} Subsequent annealing at 150 °C for 1.5 h was necessary to remove the residual weakly bound material and to promote a rearrangement of the molecules in the monolayer, improving its quality. The contact angle (SI) increases from 51° for the bare gold surface to 78° for **DAT**-treated gold. To elucidate molecular orientation, coverage and binding mode, **DAT**-functionalized gold substrates were analyzed by infrared reflection-absorption spectroscopy (IRRAS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy, scanning tunnelling microscopy (STM) and synchrotron-based X-ray photoelectron spectroscopy (XPS) as well as differential pulse voltammetry (DPV).

IRRA spectroscopy

The IR reflection-absorption spectrum of **DAT** assembled on gold (Figure 2a) is presented in the fingerprint range between

700 cm⁻¹ and 1800 cm⁻¹. It is compared to an isotropic powder spectrum of **DAT** in a KBr pellet (Figure 2b) and to a DFT-calculated IR spectrum of the molecule in the gas phase (Figure 2c), allowing the assignment of the absorption bands (Table S1). Weak IR lines (absorbance of about <0.1 %) hint at a SAM formation. The IRRA spectra in Figure 2a indicate successful cleavage of the acetyl protecting groups upon adsorption as both the C-CH₃ stretching vibration at 966 cm⁻¹ and the characteristic C=O stretching vibration at around 1700 cm⁻¹, observed for the bulk material, have disappeared. For tilt angle (α) determination^{10,62-64} we identified two absorption bands for vibrations of the top-most phenylene ring (cf. Figure S20, SI) that have transition dipole moments parallel (C-H bending vibration at 1540 cm⁻¹, p-mode, Figure 2a and 2d, blue) and orthogonal to the molecular C₂ symmetry axis (C-H wagging mode at around 782 cm⁻¹, o-mode, Figure 2a and 2d, red and Figure 2e). The molecular C₂ axis is found to be parallel to the molecular dipole μ . Without annealing, the average tilt angle of **DAT** towards the surface normal is about (30±5)°. After annealing at 150 °C, the tilt angle shrinks to (17±5)°; corresponding to a nearly orthogonal orientation of the quinoxaline with respect to the surface (for calculation details see SI, section 5.2.2).

Figure 2: IRRA spectra in the mid-infrared fingerprint range at room temperature: a) Spectrum of **DAT** adsorbed on gold after annealing at 150°C. b) Bulk spectrum of randomly oriented DAT in a KBr pellet. c) Spectrum of randomly oriented **DAT** molecules in the gas phase simulated from DFT calculations (B3LYP, 6-311+G(d,g)). The region marked in grey can be assigned to the $\nu(\text{C}=\text{O})$ vibration of the thioacetate protection group. The dashed and solid lines indicate vibrational modes with and without the influence of the protection group, respectively. Modes at 782 cm^{-1} (red) and 1540 cm^{-1} (blue) are used for the estimation of the average tilt angle α . The thin lines highlight vibrational modes with (dashed) and without (solid) the influence of the acetyl protection group. (d) Schematic drawing with the calculated α and the relevant directions. (e) The molecular dipole μ which is parallel to the C_2 symmetry axis of the molecule (see SI, section 6.2, for details).

NEXAFS spectroscopy

Complementary to IR spectroscopy, angle-dependent NEXAFS spectroscopy is an additional tool to analyze the orientation of SAMs. Representative N K-edge NEXAFS spectra of the the DAT films are shown in Figure 3 (see SI for a discussion of the C K-edge spectrum, section 5.3).

Figure 3: Representative N K-edge NEXAFS data for the as-prepared (a) and additionally annealed (b) DAT monolayers, including the spectra acquired at an X-ray incidence angle of 55° (black curves) and the difference between the spectra acquired at X-ray incidence angles of 90° and 20° (gray curves). Characteristic absorption resonances are numbered; see text for details and assignments. Horizontal dashed lines correspond to zero. The 55° N K-edge spectrum of the DAT

film (Figure 3 a) is exclusively representative of the quinoxaline moiety. This spectrum is dominated by the π^* resonance at 398.65 eV (1), accompanied by a second, much weaker π^* resonance at 401.3 eV (2) and a σ^* resonance at 406.7 eV (3). Such a spectrum is typical of quinoxaline⁶⁵ or pyrazine.⁶⁶⁻⁶⁸ The energy of the most intense resonance 1 is somewhere between those reported for poly(phenylquinoxaline) (~397.4 eV)⁶⁵ and pyrazine (401.3 eV⁶⁶ and 399.9 eV⁶⁷).

These spectra are useful to evaluate the molecular orientation in the DAT SAMs, since the quinoxaline subunit is perpendicular to the dibenzobarrelene scaffold and the $\pi(\text{C-N}^*)$ orbitals are perpendicular to the molecular plane of the quinoxaline moiety (see Figure 2d). A pronounced positive peak at the position of the resonance 1 in the differential spectrum (Figure 3b) suggests a higher intensity of this resonance for the *E* vector in the surface plane and, consequently, upright orientation of the quinoxaline moieties, corresponding to a tridentate or tetridentate adsorption of the deprotected and surface-bound DAT. A quantitative evaluation of the entire set of the N K-edge spectra within the standard formalism for a vector-like orbital,^{69,70} such as the $\pi(\text{C-N}^*)$ one, gives an average tilt angle of this orbital of $76 \pm 3^\circ$ with respect to the surface normal. This value corresponds well to the average tilt angle of $14 \pm 3^\circ$ for the quinoxaline moieties. The deviation from the ideal upright orientation might be testament to the non-ideal adsorption geometry, with a dominance of tridentate binding, as suggested by the XPS data (*vide infra*).

Annealing improves molecular orientation and the quality of the **DAT** monolayers. The N K-edge difference NEXAFS spectrum of the non-annealed **DAT**-film (Figure 3a) shows a weaker linear dichroism as compared to the annealed films (Figure 3b), with an average tilt angle of the quinoxaline subunits of $29^{\circ} \pm 3^{\circ}$ (vs. $14^{\circ} \pm 3^{\circ}$ for the annealed films). Presumably, the residual weakly bound **DAT** molecules are oriented stochastically, resulting in a higher value of the apparent tilt angle for the entire non-annealed film.

Scanning Tunneling Microscopy

To meet the requirements of STM imaging, the SAMs were prepared on Au(111) grown on a muscovite mica substrate (see SI, section 5.4 for details). A representative STM image of the **DAT** SAMs is shown in Figure 4a. Each bright dot in the image can be ascribed to an individual **DAT** molecule, leading to a surface coverage of about 0.9×10^{14} molecules per cm^2 . From the micrograph, one infers a certain narrow-range order such as (distorted)

hexagons (highlighted in white), with quite limited long-range order, presumably because of weak van-der-Waals interactions between the individual molecules.²⁴ To calculate the maximum theoretical molecular density, achieved in a tightly packed monolayer, the geometry of **DAT** obtained from its bulk single crystal structure (Figure 4b), was used as reference. By considering a sulfur (S₁)-sulfur (S₃)-distance of 12.8 Å and a methyl (C₃)-methyl (C₄)-distance of 8.5 Å (including the van-der-Waals radii of sulfur and hydrogens),⁷¹ a rectangular molecular footprint with a base area of about $1.1 \times 10^{-14} \text{ cm}^2$ was calculated, resulting in 0.9×10^{14} molecules/ cm^2 , in agreement with the STM and XPS results (see below) (1.1×10^{14} molecules per cm^2) and supported also by the work function data (see below). Also, the differential pulse voltammetry (DPV) gave the packing density value in the same range (see SI, section 5.5).

Figure 4. STM image of a **DAT** monolayer assembled on Au(111)/mica substrate; the near-range order is highlighted by the white dashed line hexagones (a). Crystal structure of **DAT** projected onto the substrate to illustrate its molecular footprint of $1.1 \times 10^{-14} \text{ cm}^2$ (b; C - black, N - blue, S - yellow, O - red) and height of 12.5 Å. The cleaved acetyl groups are transparent.

Synchrotron-based XP spectroscopy

XPS measurements shed light on the chemical composition of the interface, monolayer thickness and the binding mode of the platform molecule. By evaluation of the intensities of the characteristic XPS signals and comparing them to those of a reference sample,⁷² the effective thickness of the **DAT** films was estimated to $12.6 \pm 0.5 \text{ Å}$, in accordance with the height of the molecule, 12.5 Å (Figure 4, and Figure S28 in the SI), proving monolayer formation.⁷¹

The C 1s, N 1s and O 1s XP spectra of a **DAT**-SAM on gold also indicate successful SAM-formation (see SI, Figure S23). The most important information is provided by the S 2p

XP spectra, reflecting the binding mode of the **DAT** molecules. As shown in Figure 5, these spectra represent a superposition of two individual doublets at $\sim 162.0 \text{ eV}$ (S $2p_{3/2}$) and $\sim 163.6 \text{ eV}$ (S $2p_{3/2}$), corresponding to chemisorbed and unbound/weakly bound thiols, respectively.⁵⁷ Significantly, the S 2p spectrum of the non-annealed SAMs exhibits a rather low portion of covalent sulfur-gold bonds ($\sim 64 \%$), meaning that less than two third of the sulfur atoms (of four possible thiolate bonds of the platform) are covalently bound to the gold surface. Annealing at 150 °C increased the proportion of chemisorbed sulfur to $\sim 73 \%$ - thus statistically, 3 of 4 thiols of each molecule are covalently attached to the gold surface. As the azatriptycene scaffold

is rigid and inflexible, the presence of three Au-S-bonds within one molecule necessitates the remaining sulfur to be in close vicinity to the gold, with a similar distance as the chemisorbed thiols. The rigidity of the triply bound molecules enforces a parallel orientation of the quinoxaline with respect to the surface normal, as can be deduced from simple geometrical considerations (see SI, Figure S29). Thus, the thermal annealing step, part of our protocol, is crucial to remove the physisorbed species, resulting also in improved binding and orientation of the molecules constituting the SAM. Based on the S2p/Au4f intensity ratio and using a SAM with well-defined density as a reference, the packing density of the DAT molecules in the monolayer was estimated at $\sim 1.1 \times 10^{14}$ molecules/cm², in good agreement with the STM result (see above).

Figure 5. S 2p XP spectra of a DAT film. The spectra are decomposed in two doublets assigned to the thiolate-gold bond (red solid line) and unbound sulfur (blue solid line); a background is drawn by gray dashed line. The spectra were acquired at a primary photon energy of 350 eV.

Note that the spectroscopic data, including the S 2p spectra in particular, also fit to a coexistence of a DAT monolayer with the molecules bound to the substrate by all four anchoring groups (100%) and a certain amount of the physisorbed molecules as a "multilayer". Considering the intensities of the respective doublets in the S 2p XP spectrum of the annealed sample and the different attenuation of the photoelectron signal for the species located at the SAM-substrate (thiolate) and SAM-ambient (physisorbed) interfaces (a factor of ~ 3 at the given film thickness and kinetic energy of photoelectrons),⁷³ the maximal portion of the physisorbed molecules can be estimated to $\sim 10\%$. An intermediate situation between the monolayer and "multilayer" models is possible as well. In any case, the portion of the properly bound anchoring groups in the monolayer is equal or exceeds 75%."

Further Characterization

SAMs tune the work function of electrodes in organic electronics, while the work function shift (WFS) depends on the tilt angle of the molecular dipole. An upright alignment has the largest contribution to the WFS. However,

high tilt angles may significantly reduce the effect of a tailor-made, dipolar SAM precursor unintentionally⁶³ – utilizing dipolar multipods offers the advantage of a predetermined spatial configuration and thus maximum effect of the head group in case of orthogonality. The change in work function $\Delta\Phi$ of an electrode at a certain SAM-coverage N is described by formula (1),⁶

$$\Delta\Phi = -N \left[\frac{\mu_{\text{SAM}} \cos(\alpha)}{\varepsilon_0 \kappa_{\text{SAM}}} - \frac{\mu_{\text{M-S}}}{\varepsilon_0 \kappa_{\text{M-S}}} \right] \quad (1)$$

with the first term describing the influence of the dipole moment of the monolayer with μ_{SAM} as the dipole moment of the SAM-molecule, its tilt angle α relative to the surface normal, the permittivity of free space ε_0 and κ_{SAM} as the dielectric constant. The second term describes the contribution of the dipole originating from the metal-thiol binding to the WFS. The contribution to the WFS by the orientation of **DAT**-molecules is between 96 % ($\alpha = 17 \pm 5^\circ$ via IRRAS) and 97 % ($\alpha = 14 \pm 3^\circ$ via NEXAFS). With these findings, our calculated^{74,75} WFS of -1.05 eV fits the determined value (-1.10 eV from secondary electron cutoff),^{74,75} underlining the concept of our tetrapodal approach in terms of predictable coverage and orthogonality (see SI, section 6 for details).⁶

Conclusions

In summary, we have synthesized the novel, tetrapodal triptycene scaffold **DAT** and demonstrated its ability to form SAMs on Au(111) substrates. Multipodal SAMs often bind incompletely to the substrate, which, in case of the established tripods, does not guarantee an upright orientation of the functional head group. Using four anchors in **DAT** results in precise spatial control even in case of 75 % covalent attachment to the surface: A well-defined and vertical orientation of the functional head group of the **DAT** molecules in the SAM is verified by IRRAS and NEXAFS – three covalent gold-sulfur bonds per molecule are sufficient. Furthermore, the coverage of the SAM approached the maximum possible packing density.

DAT is synthetically accessible via diketone **4** as a modular building block, which will allow facile derivatization – virtually any *ortho*-arylenediamine (a plethora of which are commercially available) could be introduced to yield a functionalized diazatriptycene as a reliable and versatile platform for monomolecular interfacial engineering. To demonstrate SAM formation, the simplest *ortho*-phenylenediamine has been introduced in the present study. It can in particular serve as a basis for work function engineering in organic electronics, which generally relies on orientation of the molecular dipole (see SI

Figure S27 for possible structures and their calculated dipole moments). Functionalization of the **DAT** scaffold via condensation reactions to introduce dipolar groups controlling the work function will be presented in a separate publication. Additionally, our modular approach can set the basis for molecular switches and actuators operating on surfaces, SAM-based transistors or immobilized sensors/receptors, which also require a well-defined and precise orientation.

Associated Content

Supporting Information

General experimental remarks; synthetic details; crystal structure; SAM formation procedure; further details on SAM characterization via contact angle and IRRA measurements, synchrotron-based XPS and NEXAFS spectroscopy, scanning tunneling microscopy and electrochemical reductive desorption; details on work function shift; geometrical clarification.

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Notes

The authors declare no competing financial interest

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