## Molecular Tripods

# Importance of the Anchor Group Position (*Para* versus *Meta*) in Tetraphenylmethane Tripods: Synthesis and Self-Assembly Features

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**Abstract:** The efficient synthesis of tripodal platforms based on tetraphenylmethane with three acetyl-protected thiol groups in either *meta* or *para* positions relative to the central sp<sup>3</sup> carbon for deposition on Au (111) surfaces is reported. These platforms are intended to provide a vertical arrangement of the substituent in position 4 of the perpendicular phenyl ring and an electronic coupling to the gold substrate. The self-assembly features of both derivatives are analyzed on Au (111) surfaces by low-temperature ultra-highvacuum STM, high-resolution X-ray photoelectron spectroscopy, near-edge X-ray absorption fine structure spectroscopy, and reductive voltammetric desorption studies. These experiments indicated that the *meta* derivative forms a well-ordered monolayer, with most of the anchoring groups bound to the surface, whereas the *para* derivative forms a multilayer film with physically adsorbed adlayers on the chemisorbed *para* monolayer. Single-molecule conductance values for both tripodal platforms are obtained through an STM break junction experiment.

## Introduction

Tetrahedral molecules based on tetraphenylmethane have been studied extensively in recent decades. In particular, they have been used as shape-providing core motives of covalent

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201602019. <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds 2–24 containing chemical structures and numbering used for the complete peak assignment. CCDC-1475999 (22) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

organic frameworks (COFs),<sup>[1–3]</sup> porous organic polymers (POPs),<sup>[4,5]</sup> hyperbranched polymers and dendrimers,<sup>[6,7]</sup> molecular gyroscopes,<sup>[8,9]</sup> and organic light-emitting diodes (OLEDs).<sup>[10, 11]</sup> In addition, the potential of the tetrahedral synthon to act as a tripodal foot,<sup>[12]</sup> organizing and controlling the spatial arrangement of molecules in self-assembled monolayers (SAMs) on flat substrates, has been investigated. For this purpose, three of the four phenyl units are usually decorated with anchor groups interacting with the substrate, and the fourth is expected to protrude from the surface and might be substituted further. SAMs of tetraphenylmethane model compounds exposing three functional groups comprising sulfur atoms (e.g., by -CH<sub>2</sub>SH, -SAc, -SR, and -SH) to profit from their chemisorption on gold substrates have already been reported.[13-19] Depending on the type of substrate (silver, titanium oxide, indium-tin oxide), alternative anchor groups have been considered (selenium, pyridine, benzyl amine, alkyl ester, phosphonate, tertiary ammonium salts).<sup>[20-26]</sup> For binding provision on graphene surfaces by  $\pi$ - $\pi$  stacking, tetraphenylmethane-based model compounds functionalized with three "pyrene feet" were investigated.<sup>[27, 28]</sup> Structure stabilization by Van der Waals forces in monolayers, and efficient packing in SAMs, have been reported for backbones consisting of C<sub>3</sub> tetrahedral symmetric units equipped with Si or C cores.<sup>[13, 15, 29]</sup>

Our initial attempts toward tripodal model compounds were based on coordination complexes comprising both neutral  $M^{III}$  complexes<sup>[30,31]</sup> and charged tris(bipyridine)-Ru<sup>II</sup> derivatives,<sup>[32]</sup> but our recent molecular designs comprise purely organic scaffolds such as 9,9'-spirobifluorenes.<sup>[33]</sup>

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Figure 1. Structure of molecular tripods (7, 21), and proposed arrangement of 21 on a gold substrate.

Active-tail groups have been introduced to demonstrate the presence of tripodal molecules on electrodes. The concept was pioneered by Tour and co-workers with their carbazole and oli-gophenylenethylene-fullerene hybrids.<sup>[34–37]</sup>

In this paper, we compare two regioisomers of tetraphenylmethane footing architectures, namely the derivative with the three acetyl-protected thiol anchor groups in para positions (7), and the analogue with the anchor groups in meta positions (21) (Figure 1). As the active tail group facilitating their spectroscopic investigations, both model compounds expose a nitrile group in the para position, decorating the fourth remaining phenyl subunit. Gold substrates were coated with the model compounds 7 and 21, and the resulting self-assembled molecular coatings were analyzed by ultra-high-vacuum STM (UHV-STM), laboratory X-ray photoelectron spectroscopy (XPS), high-resolution XPS (HRXPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and electrochemical desorption experiments. In addition, the syntheses of both foot-structures as modular building blocks, enabling their further functionalization by cross-coupling chemistry, are reported. These modular building blocks are the boronic ester derivatives 8 and 22, as well as the iodine derivatives 10 and 24.

#### Molecular design

The rigid and well-defined tetrahedral geometry of tetraphenylmethane is ideal as a tripodal foot architecture. Three phenyl rings can be decorated with the anchor group of interest (sulfur in this case), and the fourth one is arranged perpendicular to the surface if all three anchor-group-decorated subunits interact equally with the surface. Owing to the nonconjugated character of the central sp<sup>3</sup> hybridized carbon, the molecular structures mounted on such foot architectures are expected to be arranged in a spatially well-controlled, but electronically decoupled, manner. To guarantee a tight contact of the foot structure and consequently good control over its spatial arrangement on the substrate, we decided to use arylthiol anchor groups. The remaining guestion from a molecular design viewpoint is whether the para or the meta position is better suited to provide efficient footing architectures. To address this question, we synthesized both structures (7 and 21), and studied their self-assembling behavior on gold substrates. The spacing of the anchoring group as well as the size of these specific nanostructures is a compromise between tightly packed mono- and dipodal systems and large multipodal platforms with low surface coverage. Even though functional groups allowing modular decoration of the structures (e. g., boronic acid derivatives or halides) would be very appealing from a molecular design viewpoint, our initial focus was set on tripods decorated with nitrile groups in para positions as spectroscopic markers facilitating the study of their behavior in SAMs.

### **Results and Discussion**

#### **Synthesis**

Our retrosynthetic approach is displayed in Figure 2, and consists of the assembly of the tetraphenylmethane structure in two steps. First, the three identical phenyl subunits decorated with the masked anchor group (or a substituent enabling the later introduction of the anchor group) are introduced by nucleophilic addition of lithiated species to diethyl carbonate, providing the suitably substituted trityl alcohol. The second step is a Friedel–Crafts alkylation with phenol, providing the tetraphenylmethane derivatives with one phenyl substituent exposing a phenolic hydroxyl group in the *para* position. Functional group transformation chemistry subsequently allows both the establishment of the acetyl-protected thiol anchor groups and the transformation of the phenolic hydroxy group



Figure 2. Retrosynthetic analysis of tetraphenylmethane platforms.

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into the protruding functional group of choice. The same retrosynthetic strategy can be applied for both model compounds as the position of the anchor groups is selected by the choice of the starting materials. Interestingly, in spite of the self-evident molecular design and the straightforward synthesis, none of the subunits assembled here have been reported previously.

The synthetic sequence yielding the para-substituted tetraphenylmethane derivative 7 in six steps is outlined in Scheme 1. The synthesis started with the thiol protection of commercially available 4-bromothiophenol with trimethyl(vinyl)silane through a radical reaction in the presence of 2,2'azobis(2-methylpropionitrile) (AIBN) as a radical initiator to provide 2-(trimethylsilyl)ethyl (TMSE) derivative 1 in 93% yield.<sup>[38, 39]</sup> Subsequent addition of lithiated aryl bromide 1 to diethyl carbonate afforded a mixture of benzophenone derivative 2 (24% yield) and the desired trityl alcohol 3 in 60% yield. The benzophenone derivative 2 was again reacted with an excess of lithiated aryl bromide 1 to obtain a second crop of trityl alcohol 3 in 83% yield. Then, trityl alcohol 3 was subjected to the acid-catalyzed Friedel-Crafts alkylation with phenol to provide tetraphenylmethane derivative 4 in 84% yield. The resulting phenol derivative 4 was esterified with triflic anhydride to afford triflate 5 in almost quantitative yield. Subsequently, the palladium-catalyzed cyanation of the triflate 5 with zinc and copper cyanide at 140°C provided the corresponding nitrile 6 in 93% yield. Final transprotection of the thiols was performed successfully using AgBF<sub>4</sub> and acetyl chloride (AcCl) in dichloromethane to afford the desired thioacetate 7 in 54% yield. The acetyl protection group provides improved storing and handling features of the compound, as it prohibits polymerization through intermolecular disulfide formation. Its lability allows mild and efficient deprotection prior to or during the self-assembly process on gold substrates.

Triflate **5** was converted to the more reactive iodo derivative **10** (as outlined in Scheme 2) to have in hand the modular tripodal platform bearing labile thioacetates for further functionalization through the Sonogashira cross-coupling reaction. The Miyaura borylation of aryl triflate **5** with bis(pinacolato)diboron in the presence of Pd(dppf)Cl<sub>2</sub> provided pinacol boronate **8** in 71% yield. This pinacol boron ester itself is an interesting building block, as it is suitable for the further functionalization of the tetraphenylmethane platform through Suzuki cross-coupling reactions. Then, the corresponding pinacol boronate **8** 





**Scheme 1.** Preparation of *para*-substituted tetraphenylmethane derivative **7**. Reagents and conditions: (i) trimethyl(vinyl)silane, AlBN; (ii) *tert*-BuLi, (EtO)<sub>2</sub>CO, THF; (iii) *tert*-BuLi, **1**, THF; (iv) PhOH, HCl, toluene; (v) Tf<sub>2</sub>O, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>; (vi) Zn(CN)<sub>2</sub>, CuCN, Pd(PPh<sub>3</sub>)<sub>4</sub>, DMF; (vii) AgBF<sub>4</sub>, AcCl, CH<sub>2</sub>Cl<sub>2</sub>.

was treated with copper iodide and *N*-iodosuccinimide in anhydrous DMF and toluene (2:1, v/v) using the recently reported Osuka protocol<sup>[40]</sup> to afford the aryl iodide **9** in 91% yield. The transprotection of the thiols using  $AgBF_4$  and acetyl chloride (AcCl) in dichloromethane provided the desired thioacetate **10** in 87% yield.

The same synthetic strategy was applied for the preparation of the regioisomeric *meta*-substituted tetraphenylmethane derivative **14**, which is shown in Scheme 3. The thiol of 3-bromothiophenol was protected as 2-(trimethylsilyl)ethyl derivative



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Scheme 2. Preparation of aryl iodide 10. Reagents and conditions: (i) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, dioxane; (ii) Cul, NIS, toluene, DMF; (iii) AgBF<sub>4</sub>, AcCl, CH<sub>2</sub>Cl<sub>2</sub>.

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**Scheme 3.** Synthetic attempts toward the *meta*-substituted tetraphenylmethane **14.** Reagents and conditions: (i) trimethyl(vinyl)silane, AIBN; (ii) *tert*-BuLi, (EtO)<sub>2</sub>CO, THF; (iii) *tert*-BuLi, **11**, THF; (iv) PhOH, HCI, toluene.

11 in 86% yield. Subsequent lithiation of aryl bromide 11 with tert-BuLi and stepwise addition to diethyl carbonate provided the mixture of benzophenone 12 in 39% yield and trityl alcohol 13 in 44% yield. Isolated benzophenone 12 was again treated with lithiated species to obtain a second crop of trityl alcohol 13 in 76% yield. However, subsequent acid-catalyzed Friedel-Crafts alkylation of phenol with trityl alcohol 13 did not afford the pure single tetraphenylmethane product 14. We used several Brønsted (HCl, CH<sub>3</sub>SO<sub>3</sub>H) and Lewis (BF<sub>3</sub>·Et<sub>2</sub>O) acids in combination with cosolvents (toluene, xylenes) at different temperatures (80-140°C), but all these attempts gave a complex mixture comprising regioisomers and side products, instead of the desired molecule. Even though NMR analysis indicated the presence of the desired tetraphenylmethane derivative 14, its similarity with the side products did not allow its separation.

We assumed that the increased proximity of the TMS-ethylprotected sulfanyl group in the *meta* position of the trityl alcohol handicaps its reactivity sterically, and therefore, we decided to employ less sterically bulky substituents. The new synthetic strategy leading to the *meta*-substituted tetraphenylmethane derivative **18** is outlined in Scheme 4. The synthesis started with halogen–lithium exchange of five equivalents of 1,3-dibromobenzene and its subsequent addition to diethyl carbonate to provide the desired benzophenone **15** in 93% yield. It should be noted that in the case of 1,3-dibromobenzene, the formation of the trityl alcohol derivative **16** was not observed and the reaction mixture contained almost pure benzophenone derivative **15**. Additional lithiation of 1,3-dibromobenzene and subsequent addition to the benzophenone derivative



**Scheme 4.** Synthesis of the *meta*-brominated tetraphenylmethane **18**. Reagents and conditions: (i) *n*BuLi, (EtO)<sub>2</sub>CO, THF; (ii) 1,3-dibromobenzene, *n*BuLi, THF; (iii) PhOH, HCl; (iv) Et<sub>3</sub>N, TMSCl, Et<sub>2</sub>O.

**15** afforded tris(3-bromophenyl)methanol **16** in 82% yield. After Friedel–Crafts alkylation of phenol with **16**, *meta*-brominated tetraphenylmethane derivative **17** was obtained in 88% yield. Subsequent protection of phenol as trimethylsilyl ether provided **18** in 89% yield, and allowed the further introduction of protected thiol moieties through the palladium-catalyzed reaction.

The thiol anchor groups were introduced in their TMS-ethylprotected form. Therefore, the palladium-catalyzed reaction of aryl bromide with alkyl thiol was employed,<sup>[41]</sup> through which the *meta*-brominated tetraphenylmethane derivative **18** was treated with 2-(trimethylsilyl)ethanethiol in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>, Xantphos, and Hünig's base to afford the deprotected phenolic species **14** in 92% yield upon acidic workup, as shown in Scheme 5. After triflatation of **14** with triflic anhydride, the corresponding triflate **19** was isolated in 83% yield. The palladium-catalyzed cyanation of **19** yielded nitrile **20** in 74% yield and subsequent transprotection of the thiols provided the target thioacetate **21** in 77% yield.

Analogously to the isomeric *para*-substituted platform, triflate **19** was converted to the iodo derivative **24** (Scheme 6), which is more reactive in palladium-catalyzed cross-coupling reactions than the triflate **19** itself. The Miyaura borylation of aryl triflate **19** provided the corresponding pinacol boronate **22** in 82% yield. Then, the aryl boronate **22** was substituted to the aryl iodide **23** in 83% yield, and finally, the previously mentioned transprotection of the thiols provided the desired thioacetate **24** in 55% yield.

All newly synthesized compounds were fully characterized by conventional analytical and spectroscopic methods such as <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, IR and UV/ vis spectroscopy, and elemental analysis. In addition, the identity of the tetraphenylmethane boronic acid derivative **22** was further corroborated by single-crystal XRD analysis. Single crystals of the *meta* derivative **22** were obtained by slow evapora-



**Scheme 5.** Synthesis of the *meta*-substituted tetraphenylmethane **21**. Reagents and conditions: (i) Pd<sub>2</sub>(dba)<sub>3</sub>, Xantphos, diisopropylethylamine, TMSCH<sub>2</sub>CH<sub>2</sub>SH, dioxane, H<sup>+</sup>; (ii) Tf<sub>2</sub>O, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>; (iii) Zn(CN)<sub>2</sub>, CuCN, Pd(PPh<sub>3</sub>)<sub>4</sub>, DMF; (iv) AgBF<sub>4</sub>, AcCl, CH<sub>2</sub>Cl<sub>2</sub>.



Scheme 6. Preparation of the aryl iodide 24. Reagents and conditions: (i) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, dioxane; (ii) Cul, NIS, toluene, DMF; (iii) AgBF<sub>4</sub>, AcCl, CH<sub>2</sub>Cl<sub>2</sub>.

tion of a dichloromethane/hexane solution. The solid-state structure obtained by single-crystal XRD is shown in Figure 3. Compound **22** crystallizes in the triclinic space group  $P\overline{1}$  with two molecules per unit cell. The angle between the plane made by three carbons C14, C25, C36 and the line through



Figure 3. Solid state structure of 22 obtained by single-crystal X-ray diffraction (50% probability of thermal ellipsoids). (C black, H white, O red, S yellow, Si violet, B green).

C1,C5 or C1,B1 is  $80^{\circ}$ , providing a first approximation of the arrangement of the molecular rod with respect to the surface plane.

All attempts to grow a single crystal from a tetraphenylmethane derivative with thiol groups in the *para* position failed hitherto. Details of the crystallographic data, as well as bond lengths and angles, can be found in the Supporting Information.

# Characterization of adlayers of molecular tripods 7 and 21 on the gold substrate

A detailed characterization of the adlayers of *meta* (21) and *para* (7) tripodal molecules on various gold substrates (gold single crystal, gold-coated silicon wafers, gold-coated mica, and polycrystalline gold electrode) was performed using several surface-analytical techniques including UHV-STM, laboratory XPS, synchrotron-based HRXPS and NEXAFS spectroscopy, and cyclic voltammetry (CV). Depending on the analytical technique and the nature of the corresponding sample, different sample preparation methods were applied, and during the investigation, a broad range of physical conditions was present-

ed. The variation in physical conditions ranged from low to room temperature and from UHV, through inert atmosphere, to the solid/liquid interface. The particular sample preparation details will be provided briefly at the beginning of each corresponding analytical section of the manuscript, and further method-specific details are provided in the Experimental Section.

Although the exact molecular arrangements in the different samples are expected to vary considerably owing to the differences in both sample preparation and physical conditions during characteriza-

tion, the comparison of regioisomers **7** and **21** was of interest. The main goal of this comparison was to analyze the role of the position of the anchoring groups in controlling the spatial arrangement of tripodal platforms on gold surfaces, with the aim of forming stable contacts with the surface.

#### STM analysis of the tripodal films performed at 77 K

Films of the tripodal platforms **7** and **21** for the STM investigation were prepared by immersing a sample of freshly prepared gold on mica in a solution of either *meta* (**21**) or *para* (**7**) tetraphenylmethane derivatives in a mixture of methanol/THF (3:1, v/v) containing 30% of 1 M solution of ammonia in methanol as a cleaving agent, at room temperature for 48 h (for more details see Experimental Section). After rinsing, the roughness of the prepared films was measured by STM at 77 K in UHV. In the case of the *para* derivative **7**, no signal of the tunneling current could be detected, pointing to an insulating multilayer of molecules. In contrast, in the case of the *meta* derivative **21**, STM imaging could be performed, albeit without molecular resolution. Figure 4a shows a large-scale STM image of the *meta* derivative **21** obtained at 77 K in UHV. Here, atomic steps of the Au(111) surface can be seen, separating flat terraces of

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about 150 nm in width. The inset shows a cross section of a monoatomic step with a measured height of 229 pm, close to the expected step value of 235 pm. This clearly indicates 2D growth of the molecular layer. This is in perfect agreement with the HRXPS and CV data, which indicated multilayer adsorption in the case of the *para* derivative **7** and a well-ordered monolayer in the case of the *meta* derivative **21** (see below). However, molecular resolution could not be achieved, presumably owing to contamination on top of the relatively open surface of the tripod layer.

#### STM analysis of spray-deposited tripods performed at 5.3 K

Low-coverage samples of the *meta* and *para* molecules on a clean Au(111) single crystal were prepared to gain insight into the adsorption geometry of the tripods on a well-defined metal substrate. The tripods were deposited by spraying the dissolved molecules through a pulsed valve onto the Au(111) surface. Then, after an annealing procedure, the samples were cooled to 5.3 K for the UHV-STM investigations (preparation details are provided in the Experimental Section). The advantage of this method, described in detail in our recent publication,<sup>[33]</sup> over the deposition of a droplet lies in the reduced total amount of solution that is deposited. The use of higher concentrations of molecules in the deposition solution allows further reduction of the influence of possible contamination of the solvent. We used 0.16 mM (for **21**, *meta*) and 0.20 mM (for **7**, *para*) solutions in dichloromethane. After deposition, the surface was transferred into the UHV chamber ( $p < 5 \times 10^{-10}$  mbar) and heated mildly to about 400 K for 60 min to remove remnants of the solvent and promote the deprotection of the thiol anchor groups, mediating the immobilization of the tripodal molecules on the surface. Subsequently, low-temperature STM investigations were performed at about 5.3 K to characterize the *meta* and *para* molecules on the Au(111) surface deposited by this method.

As seen in Figure 4b, deposition of a sub-monolayer amount of para molecules 7 leads to islands with long-range order and an apparent height of about 500 pm (see Figure 4c). The hexagonal order agrees with both the threefold symmetry of the molecule and the underlying lattice. Figure 4d shows an enlarged view of a unit cell (marked in black) with a lattice parameter of 3.25 nm (for details, see Supporting Information) and an area of  $(\frac{3}{4})^{0.5} \times (3.25 \text{ nm})^2 = 9.15 \text{ nm}^2$ . The precise adsorption configuration of the molecules within the unit cell, however, cannot be inferred from the STM measurements. After further annealing at 450 K for 60 min, the molecular islands rearrange and form a slightly more densely packed film (see Figure 4e,f). Here, the lattice parameter of the unit cell is 3.12 nm, corresponding to an area of 8.43 nm<sup>2</sup>. The nature of the six identical blobs that form the unit cell cannot be identified unambiguously. Intuition suggests a number of six molecules, so that each bright spot would correspond to a single molecule. Our latest measurements on similar derivatives with



Figure 4. a) Large-scale overview of the SAM of *meta*-molecule 21 (77 K). The inset shows the cross section along the white dashed line with a step height of 230 pm. b) Ordered island of *para*-molecules 7 deposited on clean Au(111) by spray deposition. c) Cross section along the white line in (b). d) Enlarged view of the area marked in (b) with the unit cell marked in black. e) Well-ordered arrangement of *para*-molecules 7 after prolonged heating. f) Enlarged view of the area marked in (e) with the unit cell marked in black. g) *meta*-Molecules 21 lined up at the step edges of the Au(111) substrate. h/i) Enlarged view of the area marked in (g)/(h) with the proposed adsorption model of the *meta*-molecule superimposed to scale. Tunneling parameters: (b)/(d): 2 V, 5 pA, (e)/(f): 2 V, 10 pA, (g)/(h): 2 V, 20 pA, (i): 0.05 V, feed back off.

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the same anchoring platforms, however, indicate the formation of molecular dimers, so interpretations of disulfide-bridged dimer species forming one bright blob in the STM image (see Figure 4e,f) should be considered, and this interpretation serves as our current working hypothesis. Assuming that each bright spot corresponds to a single molecule or a dimer, the area occupied per molecule is 1.41 or 0.70 nm<sup>2</sup> respectively. The precise adsorption configuration, however, cannot be inferred from the STM measurements.

In contrast to the para derivative 7, spray deposition of the meta derivative 21 never led to ordered molecular films or islands. Instead, these molecules adsorb preferentially along the step edges of the gold substrate, as seen in Figure 4g. We propose an array of identically adsorbed meta derivatives equally spaced with a periodicity of 1.15 nm (see enlarged view, Figure 4h). From the periodicity of 1.15 nm, we can estimate the molecular footprint as the area of an equilateral triangle to  $\frac{1}{4} \times (1.15 \text{ nm})^2 \times (3)^{0.5} = 0.57 \text{ nm}^2$ . This model is supported by the high-resolution image of a single molecule shown in Figure 4i, and agrees intuitively with the assumption of dimer formation and a slightly larger footprint of 0.70 nm<sup>2</sup> in the case of the para derivative 7. Here, the molecule can be identified by two brighter lobes directed toward the gold step edge and a third lobe that is slightly darker. The head group appears as a brighter protrusion in the center, which jumps from the left to the right during the scan with the tip close to the sample.

In summary, the low-temperature UHV studies demonstrate that both tetraphenylmethane derivatives 7 and 21 can be deposited in sub-monolayer concentration by "spraying" techniques, and after an annealing procedure, both derivatives form considerably different ordered molecular assemblies, with large islands for the para derivative 7, and rows at the step edges for the meta molecule 21. Although the dimensions of the structures' subunits match with the molecules' sizes and corroborate the molecular origin of the structures, the investigations do not allow conclusions to be drawn about the precise arrangement of the individual molecules on the substrate. The observed patterns match with tripodal structures immobilized with all three anchor groups, but the experiments cannot prove this hypothesis as the tetrahedral shape of the model compounds allows various arrangements; such proof is beyond the resolution of the experiment.

#### High-resolution X-ray photoelectron spectroscopy

For these experiments, films of the tripodal molecules were prepared by immersing a freshly prepared sample of gold on a silicon substrate into the solution of either the *meta* (**21**) or the *para* (**7**) tripodal molecule. Three different preparation procedures were tested for these films, as described in detail in the Experimental Section. On the basis of the results of the preliminary characterization by laboratory XPS as well as preliminary HRXPS and NEXAFS experiments at the synchrotron, the following optimal procedure was selected. Freshly annealed gold-coated silicon wafers (typically 10×5 mm) were immersed in a 0.25 mm solution of *meta* (**21**) or *para* (**7**) tripodal molecules in a mixture of methanol/THF (3:1, v/v) contain-

ing 30% of ammonia solution (1 M) in methanol, at room temperature for 48 h. Afterwards, the substrate was rinsed thoroughly with methanol, deionized water, and THF, and finally dried under a stream of argon. In the following, results exclusively from samples obtained by this procedure will be presented and discussed, as the alternative procedures provided films of poorer quality (see Experimental Section).

The Au4f<sub>7/2</sub>, C1s, S2p, and N1s HRXP spectra of the meta (21) and para (7) films are presented in Figure 5, along with fitting and decomposition of these spectra by characteristic emissions and doublets. The  $Au4f_{7/2}$  spectrum in Figure 5a shows noticeably lower intensity for 7/Au than for 21/Au, suggesting a higher film thickness in the former case. Indeed, according to the evaluation of the HRXPS data (see Experimental Section), the effective thicknesses of the para (7) and meta (21) films were estimated to be 2.68 and 1.83 nm, respectively. Note that the above thickness difference is much less pronounced in the C1s spectra of the tripods' films in Figure 5b, owing to the strong self-attenuation of the photoemission signal at the given kinetic energy.<sup>[42]</sup> These spectra are dominated by an intense emission at a binding energy of approximately 284.7 eV accompanied by a weak shoulder at around 286.5 eV. The dominant emission stems from the aromatic backbone, and the shoulder can be assigned to the nitrile carbon.<sup>[43]</sup> It cannot be excluded, however, that the shoulder contains a small contribution from CO, at least in the case of 7/Au, for which a small signal at approximately 288.9 eV (COO) is observed as well.

The S2p XP spectra of the tripod films in Figure 5c exhibit two doublets at around 162.0 eV and 163.6–163.9 eV (S2p<sub>3/2</sub>), assigned to the thiolate species bound to noble metal surfaces and disulfide or unbound sulfur, respectively.<sup>[44,45]</sup> The relative weights of these components are distinctly different for **21**/Au and **7**/Au. Whereas the spectrum of **21**/Au is dominated by



**Figure 5.** a) Au 4f<sub>7/2</sub>, b) C 1s, c) S 2p, and d) N 1s HRXP spectra of the *meta* (21) and *para* (7) films acquired at photon energies of either 350 or 580 eV as marked in the panels (open circles). The fitting and decomposition of the spectra are shown (thin red and blue solid lines and thick black solid line), including the respective background (thin black solid lines).

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the thiolate-related doublet (75%), the opposite is observed for 7/Au, for which the disulfide/unbound sulfur doublet is the dominant feature (85%). This suggests that the *meta* (21) film represents a monolayer, with most of the terminal –SAc moieties being deprotected and bound to the substrate as the thiolates. The respective signal is then strongly attenuated by the hydrocarbon overlayer, resulting in its comparably low intensity. In contrast, the *para* (7) film presumably represents a multilayer, with some unbound sulfur moieties buried not deep in the matrix or even close to the film-ambience interface. Accordingly, the total intensity of the S2p signal is significantly higher than in the **21**/Au case. These findings support the hypothesis of dimer formation in the case of the *para* (7) submonolayer film prepared on a Au(111) single crystal studied by low-temperature UHV-STM (see Figure 4 e,f).

The N1s XP spectra of the tripod films in Figure 5d exhibit a single emission at approximately 399.1 eV, assigned to the nitrile nitrogen. The intensity of this emission is much lower in the case of 21/Au as compared with 7/Au, suggesting much higher molecular coverage in the latter case, in agreement with the analysis of the S2p spectra. Significantly, in the case of SAM, the nitrile group is located at the film-ambience interface in the upright adsorption geometry, so the respective signal is not affected by attenuation and can be taken as a measure of the surface coverage. With respect to 4'-(pyridin-4-yl)biphenyl-4-yl)methanethiol (PyPP1)/Au, which also has nitrogen in the terminal position (see Experimental Section), the intensity of the N1s signal in 21/Au and 7/Au was estimated at approximately 14% and 59%, respectively. Accordingly, in view of the known parameters of PyPP1/Au, namely a packing density of  $4.63 \times 10^{14}$  molecules/cm<sup>2</sup> corresponding to a molecular footprint of 0.216 nm<sup>2</sup><sup>[46,47]</sup> the effective packing densities of 21/Au and 7/Au could be estimated at around  $0.65 \times 10^{14}$ and  $2.75 \times 10^{14}$  molecules/cm<sup>2</sup>, corresponding to a molecular footprint of approximately 1.5 nm<sup>2</sup> for 21/Au (because of the multilayer character of the sample, an estimation of the molecular footprint for 7/Au is not possible). An alternative evaluation of the effective packing density of 21/Au, based on the S2p/Au4f intensity ratio and using the well-defined hexadecanethiolate (HDT) SAM on Au(111) as a reference,[48,49] resulted in an effective packing density of around  $1.1 \times 10^{14}$  molecules/ cm<sup>2</sup>, corresponding to a molecular footprint of 0.9 nm<sup>2</sup>. These values are somewhat different from those derived from N1s, presumably because of the limitations of both evaluation procedures. On the other hand, the values are not too far from each other, giving a reasonable estimate of the packing density in the SAM-like 21/Au.

#### **NEXAFS** spectroscopy

NEXAFS spectroscopy provides complementary information about the tripod films, in addition to HRXPS. C and N K-edge NEXAFS spectra of the *meta* (**21**) and *para* (**7**) films acquired at an X-ray incident angle of 55° are presented in Figures 6 and 7, respectively. At this particular orientation, denoted as the "magic angle", the spectra are unaffected by orientational effects, and are therefore exclusively representative of the electronic structure of unoccupied molecular orbitals.  $^{\rm [50]}$ 

The C K-edge spectra of the tripod films in Figure 6 exhibit the characteristic absorption structure of the phenyl rings. They are dominated by a pronounced absorption resonance at approximately 285.1 eV ( $\pi_1^*$ ), accompanied by several weaker and broader resonances at  $\approx 287.6$  (mixture of R\* and C–H\*),  $\approx 288.4$  ( $\pi_2^*$ ),  $\approx 292.5$  ( $\sigma_{C-C}^*$ ),  $\approx 297.0$  ( $\sigma_{C-C}^*$ ), and  $\approx 305.0$  eV ( $\sigma_{C-C}^*$ ).<sup>[50-52]</sup> The characteristic  $\pi^*$  resonance of the nitrile moiety at around 286.7 eV<sup>[43,53]</sup> can only be traced in the spectrum of **7**/Au, as a shoulder at the absorption edge. The resonance at approximately 288.4 eV can also contain some contributions from the  $\pi^*$  feature of COOH.<sup>[50]</sup>



**Figure 6.** C K-edge NEXAFS spectra of the *meta* (21) and *para* (7) films acquired at an X-ray incident angle of 55°. The characteristic absorption resonances are marked.



**Figure 7.** N K-edge NEXAFS spectra of the *meta* (21) and *para* (7) films acquired at an X-ray incident angle of 55° (black solid curves), along with the respective difference between the spectra collected under the normal (90°) and grazing (20°) incidence geometry (gray solid curves). The spectra of the *meta* (21) films are magnified by a factor of five. The characteristic absorption resonances are marked. The horizontal dashed lines correspond to zero.

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The C K-edge spectra of the meta (21) and para (7) films differ to some extent regarding the intensity and exact shape of the absorption resonances. This difference is not surprising in view of the different coverages and distinctly different characters of these films. In particular, a spectrum similar to that of benzene<sup>[50, 51]</sup> or long-chain thio-oligophenyl SAMs<sup>[52]</sup> can be expected for the multilayer para (7) film, as is indeed observed in Figure 6. In contrast, the  $\pi^*$  resonances can be quenched to some extent in the monolayer-like meta (21) films, as observed in the respective spectrum, similar to the SAMs of phenylthiol on Au(111).<sup>[52]</sup> In addition, there can be a featureless absorption edge contribution from contamination, which presumably is present to some extent in the meta (21) and para (7) films, but is more pronounced in the former case because of the lower coverage of the target molecules. Note that, under ambient conditions, contamination is always present on the surface of the Au substrate but is mostly removed upon efficient self-assembly. The respective "self-cleaning" is, however, presumably less efficient in the case of tripod precursors owing to the comparably weak interaction between the molecular backbones, so that contamination cannot be avoided completely.

Whereas the features associated with the nitrile group are hardly visible in the C K-edge NEXAFS spectra of the tripod films, they are clearly perceptible in the N K-edge spectra of these films in Figure 7, evidencing the intact character of the adsorbed molecules. Indeed, these spectra are dominated by the characteristic double resonance of benzonitrile at approximately 398.8 and 399.75 eV. The same feature is observed in the spectra of molecular benzonitrile in the gas phase,<sup>[54]</sup> adsorbed benzonitrile,[55] and well-defined benzonitrile-terminated SAMs.<sup>[43, 53, 56, 57]</sup> The appearance of the double resonance stems from the conjugation between the  $\pi^{\ast}$  orbitals of the nitrile group and the adjacent phenyl ring. The degeneracy of the former orbital is consequently lifted, and it splits into two states with different energies, oriented either perpendicular  $(\pi_1^*)$  or parallel  $(\pi_3^*)$  to the plane of the adjacent ring.<sup>[54, 55]</sup> The delocalization of the  $\pi_1^*$  orbital over the entire benzonitrile moiety leads to the lower intensity of the respective resonance as compared to  $\pi_3^*$ , corresponding to the orbital localized at the nitrile group.

Along with the identification of the adsorbed species, NEXAFS data provide information on their orientation, based on the linear dichroism in X-ray absorption (see Experimental Section). The intensity of an absorption resonance is maximal if the orientation of the electric field vector of the linearly polarized light coincides with the transition dipole moment (TDM) of a molecular orbital of interest, and is zero if the electric field vector is perpendicular to the TDM.<sup>[50]</sup> The TDMs of the  $\pi_1^*$ and  $\pi_3^*$  orbitals are perpendicular to the axis of the benzonitrile moiety<sup>[53]</sup> and should be directed parallel to the substrate at the upright orientation of the tripod molecules. This is indeed the case for 21/Au, for which the difference between the NEXAFS spectra collected under the normal (90°) and grazing (20°) incidence geometries exhibits positive peaks at the positions of the  $\pi_1^*$  and  $\pi_3^*$  resonances (Figure 7), corresponding to the higher intensity at  $90^{\circ}$  (**E** || to the surface). In contrast, these peaks are negative in the difference spectrum of 7/ Au, corresponding to the higher intensity at  $20^{\circ}$  (**E** almost  $\perp$  to the surface). This suggests a strong molecular inclination in the multilayer *para* (**7**) film (on average), probably with a certain supramolecular arrangement involving such an inclination.

#### Surface electrochemistry

Chemisorbed *meta* (21) and *para* (7) molecules were desorbed from the gold substrate at negative applied potential during the cathodic voltammetric scan, giving a corresponding desorption peak (see Figure 8). Integration of the electric current



**Figure 8.** Cyclic voltammograms of *meta* (**21**) (left) and *para* (**7**) (right) selfassembled monolayers on gold electrode in 0.5  $\times$  NaOH aqueous electrolyte, scan rate 0.10 V s<sup>-1</sup> (black curves). Gray curves show the response of the bare gold electrode (i.e., with no adlayer) under otherwise the same conditions.

gives the electric charge Q, which, according to Equation (1), provides information on the surface concentration of the adsorbed molecules,  $\Gamma$ .<sup>[58]</sup>

$$\Gamma = (Q - Q_{dl}) / nFA \tag{1}$$

For the meta (21) derivative, assuming negligible doublelayer charging current  $(Q_{dl} = 0)$  and the number of transferred electrons n equal to three (one for each thiolate anchor), a value of  $(4.9\pm0.2)\times10^{-10}\,\text{mol}\,\text{cm}^{-2}$  is obtained for the surface concentration  $\Gamma$ . This represents  $(3.0 \pm 0.2) \times$ 10<sup>14</sup> molecules cm<sup>-2</sup> and leads to an area occupied by one molecule of 0.34 nm<sup>2</sup> molecule<sup>-1</sup>. This value is in good agreement with that obtained from an STM image of individual molecules  $(0.57 \text{ nm}^2 \text{molecule}^{-1})$  as well as with the area of a triangle made by three outer para hydrogen atoms H17, H28, H39 (0.32 nm<sup>2</sup>molecule<sup>-1</sup>) of the similar meta derivative 22 obtained from single-crystal X-ray diffraction (Figure 3 and corresponding X-ray data in Supporting Information), and would provide even better agreement once the value of the double layer charge  $Q_{dl}$  is known and taken into account. In any case, the above result confirms unequivocally that meta (21) is anchored to the gold substrate through three thiolate bonds forming a chemisorbed compact monolayer (consistent with STM images in Figure 4a). This finding is crucial if the well-ordered SAMs of meta (21) tripods are to be used in further applications.

Integration of the total voltammetric response obtained upon desorption of the *para* (7) derivative led to a surface concentration value of  $(5.9\pm0.4)\times10^{-10}$  mol cm<sup>-2</sup> or  $(3.6\pm0.3)\times10^{14}$  molecules cm<sup>-2</sup>, which is slightly higher than the value ob-



the meta (21) derivative  $[(3.0 \pm 0.2) \times$ tained for 10<sup>14</sup> molecules cm<sup>-2</sup>] using the same assumptions for the  $\Gamma$  calculation. A small voltammetric prewave at -0.85 V was observed reproducibly during desorption of the para (7) derivative (Figure 8, right). This could indicate the presence of an additional, physically adsorbed adlayer on the chemisorbed para (7) monolayer<sup>[59]</sup> or desorption of the disulfide dimers of the para (7) bound to the gold surface by free thiol(s). The main desorption peak for the para (7) derivative was observed at a more negative potential than for the meta (21) derivative (Figure 8), indicating stronger interaction of (7) with the underlying gold substrate.<sup>[60]</sup> At this point we cannot tell how many electrons are being transferred (as we cannot exclude desorption of the para (7) dimer) and thus provide additional information on the composition of the film from the desorption data.

#### Single-molecule conductance measurements

The scanning tunneling microscopy break junction (STM-BJ) technique<sup>[61]</sup> was applied to investigate the charge transport through the tetraphenylmethane-based molecular tripods. The STM-BJ was formed repeatedly by perpendicular movement of the electrochemically etched gold tip (0.25 mm wire, 99.99% Goodfellow, UK) toward the gold substrate immersed in a 1 mm solution of 7 or 21 in mesitylene, which was spiked with triethylamine to achieve in situ deprotection of the anchoring groups. All conductance-distance traces obtained during molecular junction elongation were converted cumulatively to a 1D conductance histogram. Very similar 1D conductance histograms of  $log(G/G_0)$  were obtained for both molecules, showing a broad conductance feature, which can be fitted by two peaks (see Figure 9). For the para derivative (7), these two peaks give high and low conductance values equal to  $G_{\rm H}\!=\!10^{-3.16\pm0.46}G_{\rm 0}$  and  $G_{\rm L}\!=\!10^{-4.07\pm0.59}G_{\rm 0}\!,$  and for the meta derivative (21) values of  $G_{\rm H}=10^{-3.32\pm0.54}G_{\rm 0}$  and  $G_{\rm L}=$  $10^{-4.05\pm0.40}G_0$ , respectively. The low conductance values are almost identical for both molecules, whereas the high conductance value is slightly higher for the para derivative (7). It was proposed recently that a low conductance value  $G_i$  may be caused by a weakly conducting cofacial  $\pi$ - $\pi$  stacked dimer formation, whereas G<sub>H</sub> represents true single-molecule conductance.<sup>[62]</sup> On the other hand, it was also shown that molecules



**Figure 9.** Logarithmically binned 1D histogram of log( $G/G_0$ ) for meta (21) (left) and para (7) (right) molecules in mesitylene constructed from all data points;  $V_{\text{bias}} = 0.13$  V, retraction rate = 36 nm s<sup>-1</sup>, bin size 0.005. Conductance is presented in units of quantum conductance,  $G_0 = 77.5 \, \mu\text{S}$ .

terminated by nitrile anchoring groups on each end form a symmetric junction that breaks in such a way that the current-distance curves exhibit two distinct slopes in the current plateau region (just before junction breaking). These two slopes lead to a broad peak in the 1D conductance histogram that can be fitted by two conductance values, indicating the conductance of a single molecule in distinctly different stages of the junction formation.<sup>[63]</sup> Similar behavior was observed in Figure 9, confirming that the junction breaks on the side of the nitrile contacting group whereas the tripod anchor represents a very robust contact.

It is known from the literature<sup>[64]</sup> that single-molecule conductance depends strongly on the type of anchoring group, and that the probability of junction formation and its stability decrease on going from the SH to CN anchoring group, with the latter having lower binding energy. For example, in a series of tolanes, symmetrically terminated on both sides by either SH or CN groups, the reported conductance and junction formation probability for the SH-terminated molecule were  $G_{\rm H} =$  $10^{-2.7}G_0$  and approximately 90%, respectively, whereas for the CN-terminated one the values were  $G_{\rm H} = 10^{-4.6}G_0$  and approximately 70%, respectively.<sup>[64]</sup> Previously reported junction evolution studies  $^{\scriptscriptstyle [63, 64]}$  lead us to propose that the conductance corresponding to  $G_H$  values is given predominantly by the differences on the side of thiolate–gold anchor, whereas  $G_{L}$  is related to the CN-gold anchor. Note that the slightly higher  $G_{\rm H}$ values obtained for the para (7) compared to the meta (21) molecules are in agreement with theoretical calculations, which suggest higher conductance for para substitution on the aromatic ring than for substitution in the *meta* position.<sup>[65]</sup>

#### Conclusion

In summary, two regioisomeric tripodal model compounds consisting of a tetraphenylmethane backbone and three acetyl-protected thiol substituents directly mounted on the phenyl ring in either para (7) or meta position (21) have been synthesized and fully characterized, and their self-assembly behavior has been investigated in different coverage and preparation regimes through a variety of experimental techniques, including low-temperature UHV-STM, HRXPS, NEXAFS spectroscopy, and reductive voltammetric desorption experiments. The modular syntheses, introducing the protruding functionality in the para position of the fourth phenyl ring late in the sequence, enabled the provision not only of the model compounds 7 and 21 exposing a nitrile group, but also tripodal derivatives exposing other functional groups, for example, for transition-metal-catalyzed coupling chemistry such as the iodine derivatives (10 and 24) or the boronic acid esters (8 and 22). The electronic conductance of the model compounds 7 and 21 was investigated through single-molecule transport studies.

The experimental data obtained from the different techniques, and above all, the predominant thiolate signal in the S2p XP spectra, suggest consistently that the adsorption of the *meta*-substituted model compound **21** on Au(111) by the standard immersion procedure results in the formation of

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a well-defined SAM-like film with the majority of its constituents attached with all three legs to the gold surface. Other findings supporting a monolayer character for this compound are the intensity of the  $Au4f_{7/2}$  HRXPS signal, the UHV-STM data, the N1s XP data, and the results of the electrochemical experiments. This interpretation was also supported by the N K-edge NEXAFS data, suggesting an upright orientation for the nitrile groups in **21**/Au. Sub-monolayer samples prepared by spraying solutions of **21** into the UHV showed parallel rows of paired molecules at the gold step edges in the STM analysis, which allowed analysis of the dimensions of the deposited molecules.

The observations for the regioisomer **7** with the thiol anchor groups is the *para* position suggest the formation of molecular multilayers, with a lower degree of orientational order compared with **21**. The multilayer nature of these films is reflected in their thickness, as follows from the analysis of the intensity of the Au 4f<sub>7/2</sub> HRXPS signal as well as from the insulated character of these films as observed in the UHV-STM experiments. A large fraction of the unbound docking groups was observed in the S 2p XP spectrum, and no preferred orientation of the nitrile group was found in the NEXAFS data. However, deposited as a sub-monolayer in the UHV-STM experiment, large ordered domains consisting of molecules ordered in hexagonal tiles were observed. Although the experiment does not allow conclusions concerning the orientation of the molecule at the surface, the dimensions of the molecular footprint were obtained.

Single-molecule conductance was measured for both tripodal molecules 7 and 21 through STM break junction experiments. Comparable values were obtained, which might point to the central sp<sup>3</sup> hybridized C atom as the structural feature controlling the electronic coupling irrespective of the connection of the structure to the substrate.

Currently, we are exploring further to what extent the molecular arrangement on the substrate surface can be controlled by the deposition method, and the size of the molecular structures that can be mounted on these platforms.

#### **Experimental Section**

#### Materials

All starting materials and reagents were obtained from commercial suppliers and used without further purification. TLC was performed on silica gel 60 F<sub>254</sub> plates; spots were detected by fluorescence quenching under UV light at 254 nm. Column chromatography was performed on silica gel 60 (0.040-0.063 mm). All experimental manipulations with anhydrous solvents were performed in flamedried glassware under an inert argon atmosphere. Degassed solvents were obtained through three freeze-pump-thaw cycles. Tetrahydrofuran, toluene, and diethyl ether were dried and distilled from sodium/benzophenone under an argon atmosphere. Dichloromethane and triethylamine were dried and distilled from CaH<sub>2</sub> under an argon atmosphere. Ultrapure deionized (DI) water with a minimum resistivity of 18.2 M $\Omega$  cm was obtained by means of a Milli-Q Integral 5 water purification system. All glassware for the electrochemical experiments was cleaned in boiling 20% nitric acid and washed copiously in ultrapure water. 4-Bromo-1-[2-(trimethylsilyl)ethylsulfanyl]benzene 1<sup>[38,39]</sup> and 3-bromo-1-[2-(trimethylsilyl)ethylsulfanyl]benzene 11<sup>[33]</sup> were prepared according to the published procedures.

#### Equipment and measurements

All NMR spectra were recorded at 25 °C in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (500.16 MHz) spectra were referenced to TMS as internal standard  $(\delta_{\rm H}=0 \text{ ppm})$  or to the solvent residual proton signal (CDCl<sub>3</sub>,  $\delta_{\rm H}=$ 7.26 ppm; CD<sub>2</sub>Cl<sub>2</sub>,  $\delta_{\rm H}$  = 5.32 ppm). <sup>13</sup>C NMR (125.78 MHz) spectra with total decoupling of protons were referenced to the solvent (CDCl<sub>3</sub>,  $\delta_{\rm H} =$  77.23 ppm; CD<sub>2</sub>Cl<sub>2</sub>,  $\delta_{\rm H} =$  54.00 ppm). <sup>19</sup>F{<sup>1</sup>H} NMR (470.57 MHz) spectra were referenced to CFCl<sub>3</sub> as an external standard in a coaxial capillary ( $\delta_{\rm F}$  = 0.00 ppm). UV/Vis spectra were recorded with a UV/Vis spectrometer in a 1 cm quartz cell at ambient temperature (excitation coefficients are given below in units of Lmol<sup>-1</sup> cm<sup>-1</sup>). HRMS spectra were obtained with an ESI-TOF mass spectrometer. IR spectra were measured in KBr pellets. Analytical samples were dried at 40-100 °C under reduced pressure  $(10^{-2} \text{ mbar})$ . Melting points were measured with a melting point apparatus. Elemental analyses were obtained using an elemental analyzer.

#### Film characterization

The SAMs for the STM characterization at 77 K were prepared on freshly annealed gold-coated (300 nm) mica substrates (typically 5×5 mm), which were purchased from Georg-Albert-PVD, Germany. The substrates were immersed in a solution (0.25 mm) of meta (21) or para (7) tripodal molecules in a mixture of methanol/THF (3:1, v/v) containing 30% of a 1 M solution of ammonia in methanol as cleaving agent, at room temperature for 48 h. The samples were rinsed thoroughly with methanol, DI water, and THF, dried under a stream of argon, and placed into the UHV-STM chamber. The SAMs for the STM characterization at 5.3 K were prepared on a Au(111) single crystal, which was cleaned by repeated cycles of argon ion sputtering and annealing to 720 K. The tripodal molecules 7 and 21 were deposited onto the substrate surface by spray deposition. For this purpose, the substrate was transferred to a separate vacuum chamber with a pressure of approximately 5 mbar. A droplet of 7 or 21 dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.16 mm for meta derivative 21 and 0.20 mm for para derivative 7) was sprayed into the chamber by opening the pulse valve for 10 ms. Thus, a mist containing the dissolved molecules was deposited onto the substrate. The sample was then transferred to UHV and annealed mildly at T=400 K for 60 min to remove remaining solvent molecules. Subsequently, the sample was transferred to a custom-built STM setup. STM images were measured in constant current mode at 5.3 K.

The samples for the spectroscopic characterization were prepared on freshly annealed gold-coated Si(100) wafers (typically  $10 \times$ 5 mm) with 5 nm Ti and 100 nm Au. These substrates were purchased from Georg-Albert-PVD, Germany. Three different preparation procedures for the formation of the tripod films were tried. In the first procedure, the substrates were immersed in a 0.25 mм solution of meta (21) or para (7) tripodal molecules in a mixture of methanol/THF (3:1, v/v) containing 30% of a 1м solution of ammonia in methanol as cleaving agent, at room temperature for 48 h. In the second procedure, the samples were immersed in a 0.5 mm solution of tripodal molecules in the mixture of methanol/THF (3:1, v/v) at 50 °C for 48 h. Finally, in the third procedure, the samples were immersed in a 0.5 mm solution of tripodal molecules in THF containing 15% triethylamine as cleaving agent, at room temperature for 48 h. In all three cases, the substrates were rinsed thoroughly with methanol, DI water, and THF, and then dried under a stream of argon. The first procedure was found to

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be the most suitable and reliable. Consequently, only samples prepared by this procedure were used for the subsequent HRXPS and NEXAFS experiments at the synchrotron.

Along with the SAMs of tripodal molecules **7** and **21**, monolayers of hexadecanethiol (HDT) and 4'-(pyridin-4-yl)biphenyl-4-yl)methanethiol (PyPP1) were prepared on a Au(111) substrate following the literature procedures.<sup>[47,66]</sup> These monolayers were used as references to calculate the effective thicknesses (HDT) and packing densities (HDT and PyPP1) of the triad films. Significantly, the PyPP1 monolayer has a nitrogen atom in the terminal position, similarly to the triad films in the proper adsorption geometry. The structure of this monolayer is similar to the basic  $\sqrt{3} \times \sqrt{3}$  arrangement in the alkanethiolate SAMs,<sup>[66]</sup> with a packing density close to 4.63× 10<sup>14</sup> molecules cm<sup>-2</sup>, corresponding to 0.216 nm<sup>2</sup> molecule<sup>-1.[46,47]</sup>

The SAMs of the *meta* (21) and *para* (7) tripodal molecules were characterized by laboratory XPS, HRXPS, and NEXAFS spectroscopy. The laboratory XPS measurements were used for a preliminary screening only, to optimize the preparation procedure. All experiments were performed at room temperature. The spectroscopy measurements were conducted under UHV conditions at a base pressure  $< 1.5 \times 10^{-9}$  mbar. Special care was taken to avoid damage induced by X-rays.<sup>[44,67]</sup>

Laboratory XPS measurements were performed using a MgK<sub>a</sub> X-ray source (1253.6 eV) and a dedicated spectrometer (MAX200, Leybold–Heraeus). The spectra were acquired in normal emission geometry with an energy resolution of around 0.9 eV. The X-ray source was operated at a power of 200 W and positioned approximately 1.5 cm away from the samples. The recorded spectra were normalized to the transmissions function of the spectrometer, and the binding energy scale was referenced to the Au4f<sub>7/2</sub> peak of clean gold at 84.0 eV.<sup>[68]</sup>

The HRXPS experiments were performed at the D1011 beamline (bending magnet) at the MAX II storage ring of the MAX-IV synchrotron radiation facility in Lund, Sweden. The spectra were acquired in normal emission geometry at photon energies of 350 and 580 eV, depending on the acquisition range. The energy resolution was better than 100 meV, allowing clear separation of individual spectral components. The binding energy scale was referenced to the Au4f<sub>7/2</sub> peak of clean gold at 84.0 eV.<sup>[66]</sup>

XP and HRXP spectra were fitted by symmetric Voigt functions and a Shirley-type background. To fit the  $S2p_{3/2r1/2}$  doublet we used two peaks with the same full-width at half-maximum (fwhm), the standard<sup>[68]</sup> spin-orbit splitting of approximately 1.18 eV (verified by fit), and a branching ratio of 2 ( $S2p_{3/2}/S2p_{1/2}$ ). The fits were performed self-consistently, that is, the same fit parameters were used for identical spectral regions.

HRXPS data were used to calculate the effective thicknesses of the triad films. A standard procedure was used,<sup>[69]</sup> based on the C1s/ Au4f intensity ratio and an SAM (HDT/Au) of well-defined thickness (1.84 nm) as a reference. Attenuation length values characteristic of densely packed alkanethiolate SAMs on Au(111) were used.<sup>[70]</sup>

The NEXAFS measurements were performed at same beamline as the HRXPS experiments. The spectra were acquired at the carbon and nitrogen K-edges in the partial electron yield mode with retarding voltages of -150 and -300 V, respectively. Linear polarized synchrotron light with a polarization factor of about 95% was used. The energy resolution was better than 100 meV. The incidence angle of the primary X-rays was varied from 90° (E-vector in the surface plane) to 20° (E-vector nearly normal to the surface) in steps of 10°–20° to monitor the orientational order within the tripod films. This approach is based on the linear dichroism in X- ray absorption, that is, the strong dependence of the cross section of the resonant photoexcitation process on the orientation of the electric field vector of the linearly polarized light with respect to the molecular orbital of interest.<sup>[50]</sup>

The raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. The energy scale was referenced to the most intense  $\pi^*$  resonance of highly oriented pyrolytic graphite (HOPG) at 285.38 eV.<sup>[71]</sup>

Single-molecule conductance was measured with an original STM tubular scanner Agilent 5500 Scanning Probe Microscope with an in-house-implemented current-to-voltage converter circuit with a wide dynamic range.<sup>[72]</sup> Current-time curves were converted to conductance-distance curves, and corresponding histograms were constructed using a combination of software developed in-house<sup>[73]</sup> and OriginPro. A logarithmic bin size of 0.005 was used for the construction of 1 D histograms of  $\log(G/G_0)$  values from the original data without any selection, in which *G* is the conductance, presented in units of quantum conductance  $G_0 = 77.5 \, \mu S.^{[74]}$ 

For electrochemical desorption studies, monolayers of *meta* derivative **21** and *para* derivative **7** were prepared on gold bead electrodes (area 0.17–0.21 cm<sup>2</sup>) by deposition from a 0.2 mM solution in ethanol containing triethylamine (10% v/v ratio) at 60 °C for 16 h. Subsequently, the electrodes were rinsed copiously with pure ethanol. Cyclic voltammograms were measured using a Potentiostat/ Galvanostat PGSTAT12 at a scan rate of 0.10 V s<sup>-1</sup>. Desorption was performed in 0.5 M NaOH in ultrapure water in a three-electrode system containing a gold bead working electrode in a hanging meniscus arrangement and pseudo-reference and auxiliary (both gold) electrodes.

#### Tris{4-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methanol (3)

Method A: A dry, argon-flushed 100 mL Schlenk flask was charged with 1 (3.76 g, 13 mmol), and anhydrous THF (35 mL) was added. The solution was cooled to -78 °C and tert-BuLi (17.8 mL, 26 mmol, 15% in pentane) was added dropwise over 20 min. The reaction mixture was stirred at  $-78\,^\circ\text{C}$  for 2 h under argon. In a second 100 mL Schlenk flask, diethyl carbonate (0.44 mL, 3.71 mmol) was diluted with anhydrous THF (5 mL) under an inert atmosphere and cooled to -78 °C. The solution of lithiated species was added slowly through a cannula into the flask containing diethyl carbonate solution; after 1 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 16 h. The reaction mixture was quenched with saturated NH<sub>4</sub>Cl solution (100 mL). The aqueous layer was washed with  $CH_2CI_2$  (2× 100 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO4, and filtered. All volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (300 g) in hexane/EtOAc (9:1) to afford pure **3** (1.46 g) as a yellowish solid in 60% yield ( $R_f = 0.45$ , hexane/EtOAc=9:1) and pure 2 (0.4 g) as a white solid in 24% yield ( $R_f = 0.54$ , hexane/EtOAc = 9:1).

For **3**: m.p. 121–131 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.04 (s, 27 H), 0.92–0.96 (m, 6H), 2.71 (s, OH), 2.94–2.96 (m, 6H), 7.16–7.18 (m, 6H), 7.22–7.23 ppm (m, 6H); <sup>13</sup>C NMR (125.88 MHz, CDCl<sub>3</sub>):  $\delta$  = -1.5, 17.0, 29.4, 81.6, 128.0, 128.5, 136.9, 144.1 ppm; IR (KBr)  $\tilde{v}$  = 3446 (s), 3025 (w), 2952 (s), 1594 (m), 1490 (s), 1417 (m), 1249 (s), 1161 (m), 838 (s), 693 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 269 nm (43186 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C<sub>34</sub>H<sub>52</sub>OS<sub>3</sub>Si<sub>3</sub>Na: 679.2289 [*M*+Na]<sup>+</sup>; found: 679.2380; elemental analysis calcd (%) for C<sub>34</sub>H<sub>52</sub>OS<sub>3</sub>Si<sub>3</sub> (656.25): C 62.14, H 7.98; found: C 62.23, H 8.05.

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For **2**: m.p. 71–74 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.02 (s, 18H), 0.97–1.00 (m, 4H), 3.02–3.06 (m, 4H), 7.29–7.31 (m, 4H), 7.70–7.71 ppm (m, 4H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$  = -1.5, 16.7, 28.4, 126.5. 130.7, 134.4, 144.5, 195.1 ppm; IR (KBr)  $\bar{\nu}$  = 3037 (w), 2952 (s), 1657 (s), 1553 (s), 1401 (m), 1288 (s), 1088 (s), 830 (s), 692 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 329 nm (29245 mol<sup>-1</sup>dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C<sub>23</sub>H<sub>34</sub>OS<sub>2</sub>Si<sub>2</sub>Na: 469.1378 [*M*+Na]<sup>+</sup>; found: 469.1482; elemental analysis calcd (%) for C<sub>23</sub>H<sub>34</sub>OS<sub>2</sub>Si<sub>2</sub> (446.16): C 61.83, H 7.67; found: C 61.59, H 7.88.

Method B: In a 100 mL Schlenk flask, 1 (1.16 g, 4.01 mmol) was dissolved in anhydrous THF (12 mL) under argon, cooled to -78 °C, and degassed. Then, tert-BuLi (5.6 mL, 8.24 mmol, 15% in pentane) was added dropwise over 25 min and the resulting mixture was stirred at -78°C for 2 h. In a second 100 mL Schlenk flask, 2 (0.9 g, 2.02 mmol) was dissolved in THF (8 mL) under argon, and cooled to -78°C. The solution of lithiated species was added slowly through a cannula into the flask containing the solution of 2. The yellow solution was stirred at -78 °C for 2 h, then allowed to warm to room temperature and stirred for an additional 12 h. The reaction mixture was quenched with saturated NH<sub>4</sub>Cl solution (100 mL). The aqueous layer was washed with  $CH_2CI_2$  (2×150 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (200 g) in hexane/EtOAc (9:1) to yield 3 (1.1 g, 83%) as a yellowish solid.

#### 4-(Tris{4-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)phenol (4)

A 100 mL two-necked round-bottomed flask was charged with 3 (0.69 g, 1.05 mmol), phenol (1.97 g, 21 mmol), and toluene (10 mL) under argon, and a few drops of concentrated HCl were added. The reaction mixture was heated at 120 °C for 14 h under argon. After cooling to room temperature, the navy blue reaction mixture was diluted with toluene (120 mL) and guenched with NaOH solution (2 m, 160 mL). The combined organic layer was washed with water (150 mL), dried over MgSO4, and filtered. All volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (150 g) in hexane/EtOAc (5:1) to afford **4** (0.65 g) as an orange solid in 84% yield.  $R_{\rm f} = 0.26$ (hexane/EtOAc = 9:1); m.p. 98–101 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta =$  0.03 (s, 27 H), 0.92–0.95 (m, 6 H), 2.93–2.96 (m, 6 H), 4.79 (s, OH), 6.69-6.71 (d, J=8.6 Hz, 2H), 7.00-7.02 (d, J=8.65 Hz, 2H), 7.06-7.08 (m, 6H), 7.14–7.15 ppm (m, 6H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.6$ , 17.0, 29.3, 63.4, 114.5, 127.4, 131.6, 132.4, 135.3, 139.0, 144.3, 153.8 ppm; IR (KBr)  $\tilde{v} = 3403$  (s), 3022 (w), 2951 (s), 1591 (m), 1488 (s), 1428 (m), 1248 (s), 837 (s), 692 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 271 nm (74485 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C40H56OS3Si3Na: 771.2698 [M+Na]+; found: 771.2609; elemental analysis calcd (%) for  $C_{40}H_{56}OS_{3}Si_{3}$  (732.28): C 65.52, H 7.70; found: C 65.30, H 7.76.

#### 4-(Tris{4-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)phenyl trifluoromethanesulfonate (5)

Trifluoromethanesulfonic anhydride (0.22 mL, 1.3 mmol) was added dropwise to a solution of 4 (0.56 g, 0.76 mmol) in dry triethylamine (0.2 mL, 1.4 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at -78 °C under an argon atmosphere. The solution was stirred for 6 h at -78 °C, and then allowed to warm to room temperature and stirred for an additional 10 h, before being quenched with water (100 mL). The aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> (2×150 mL). The combined organic

layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (130 g) with hexane/EtOAc (9:1) as an eluent to yield 0.64 g (97%) of **5**.  $R_f$ =0.88 (hexane/EtOAc=9:1); m.p. 98–101°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.05 (s, 27 H), 0.93–0.96 (m, 6H), 2.94–2.98 (m, 6H), 7.04–7.05 (m, 6H), 7.14–7.17 (m, 8H), 7.27–7.28 ppm (d, J=8.85 Hz, 2H), <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$ =-1.6, 16.9, 29.1, 63.7, 120.5, 127.4, 131.4, 132.9, 136.1, 143.1, 147.2, 147.8 ppm; <sup>19</sup>F NMR (470.57 MHz, CDCl<sub>3</sub>):  $\delta$ =-72.92 ppm; IR (KBr)  $\ddot{v}$ =3025 (w), 2953 (s), 1557 (m), 1490 (s), 1429 (s), 1250 (s), 1214 (s), 1141 (s), 812 (s), 694 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ )=273 nm (33 589 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C<sub>41</sub>H<sub>55</sub>O<sub>3</sub>S<sub>4</sub>Si<sub>3</sub>FNa: 887.2186 [*M*+Na]<sup>+</sup>; found: 887.2121; elemental analysis calcd (%) for C<sub>41</sub>H<sub>55</sub>O<sub>3</sub>S<sub>4</sub>Si<sub>3</sub>F (864.23): C 56.91, H 6.41; found: C 56.97, H 6.55.

#### 4-(Tris{4-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)benzonitrile (6)

A 50 mL pressure tube was charged with triflate 5 (0.25 g, 0.29 mmol), zinc cyanide (0.14 g, 1.19 mmol), copper(I) cyanide (0.026 g, 0.29 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.034 g, 0.029 mmol) and anhydrous DMF (8 mL) under argon. The tube was sealed and stirred at 140°C for 16 h. The solution was cooled to room temperature, and the resulting solution was quenched with Na<sub>2</sub>CO<sub>3</sub> (60 mL). The aqueous layer was washed with  $CH_2CI_2$  (2×150 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. All volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (70 g) in a mixture of hexane/EtOAc (9:1), yielding 0.2 g of 6 as a white powder in 93% yield.  $R_f = 0.44$  (hexane/EtOAc = 9:1); m.p. 156–158 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.04$  (s, 27 H), 0.92–0.96 (m, 6H), 2.93–2.97 (m, 6H), 7.03–7.05 (m, 6H), 7.15–7.17 (m, 6H), 7.32-7.34 (d, J=8.85 Hz, 2H), 7.53-7.55 ppm (d, J=8.5 Hz, 2H), <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.5$ , 16.9, 29.1, 64.3, 110.2, 119.0, 127.4, 131.4, 131.6, 131.8, 136.3, 142.7, 152.2 ppm; IR (KBr)  $\tilde{v}$  = 3024 (w), 2953 (s), 2231 (m), 1605 (m), 1489 (s), 1401 (w), 1248 (s), 1094 (s), 859 (s), 694 cm  $^{-1}$  (w); UV/Vis (CH\_2Cl\_2):  $\lambda_{\rm max}$  ( $\!\epsilon\!$ ) = 224 (13100), 270 nm (23 341 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: m/z calcd for C<sub>41</sub>H<sub>55</sub>OS<sub>3</sub>Si<sub>3</sub>NNa: 764.2697 [*M*+Na]<sup>+</sup>; found: 764.2548; elemental analysis calcd (%) for  $C_{41}H_{55}OS_{3}Si_{3}N$  (741.28): C 66.34, H 7.47, N 1.89; found: C 66.56, H 7.61, N 1.92.

#### S,S',S''-{4,4',4''-[(4-Cyanophenyl)methanetriyl)]tris(benzene-4,1-diyl)} tris(thioacetate) (7)

In a 50 mL Schlenk flask, tetraphenylmethane 6 (150 mg, 0.20 mmol) was dissolved in a mixture of dry CH<sub>2</sub>Cl<sub>2</sub> (16 mL) and acetyl chloride (1.6 mL) under argon. The solution was treated with AgBF<sub>4</sub> (0.2 g, 1.02 mmol), and the green suspension was stirred at room temperature for 12 h. The completion of the reaction was checked by TLC (hexane/EtOAc=3:1). The reaction mixture was diluted with dichloromethane (100 mL) and poured slowly into a saturated solution of NaHCO3 (60 mL). The precipitate was filtered through a pad of Celite, washed with CH<sub>2</sub>Cl<sub>2</sub>, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (150 g) with hexane/EtOAc (3:1) to yield 62 mg (54%) of **7** as a white powder.  $R_f = 0.11$  (hexane/EtOAc = 3:1); m.p. 202-204 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.42$  (s, 9H), 7.21–7.22 (m, 6H), 7.32-7.34 (m, 6H), 7.36-7.37 (d, J=8.5 Hz, 2H), 7.56-7.58 ppm (d, J=8.5 Hz, 2 H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 30.47$ , 65.05, 110.7, 118.7, 126.9, 128.63, 128.69, 131.6, 131.7, 131.9, 134.05, 146.1, 150.9, 193.7 ppm; IR (KBr)  $\tilde{v} = 3029$  (w), 2920 (s), 2227 (m), 1704 (s), 1603 (w), 1486 (m), 1396 (m), 1194 (w), 1117 (m), 820 (s),

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618 cm<sup>-1</sup> (s); UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 223 (31640), 250 nm (27521 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI (+) HRMS: *m/z* calcd for C<sub>32</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>3</sub>Na: 590.0889 [*M*+Na]<sup>+</sup>; found: 590.0883; elemental analysis calcd (%) for C<sub>32</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>3</sub> (567.10): C 67.70, H 4.44, N, 2.47; found: C 67.89, H 4.53, N 2.58.

#### 4-(Tris{4-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)phenylboronic acid pinacol ester (8)

A 50 mL pressure tube was charged with triflate 5 (0.65 g, 0.75 mmol), anhydrous potassium acetate (0.22 g, 2.24 mmol), bis(pinacolato)diboron (0.29 g, 1.14 mmol), Pd(dppf)Cl<sub>2</sub> (0.061 g, 0.075 mmol), and dry dioxane (15 mL) under argon. The tube was sealed and stirred under at 120 °C for 16 h. The reaction mixture was cooled, then diluted with dichloromethane (200 mL) and washed with water (100 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (130 g) with hexane/EtOAc (9:1) to provide 0.45 g of 8 as a yellow powder in 71% yield.  $R_f = 0.6$  (hexane/EtOAc = 9:1); m.p. 174–175°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.03$  (s, 27 H), 0.91–0.95 (m, 6 H), 1.32 (s, 12 H), 2.92-2.96 (m, 6H), 7.08-7.09 (m, 6H), 7.13-7.15 (m, 6H), 7.19-7.20 (d, J = 7.8 Hz, 2H), 7.67–7.69 ppm (d, J = 8 Hz 2H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.5$ , 17.0, 25.1., 29.3, 64.3, 84.0, 127.5, 130.5, 131.5, 131.6, 134.2, 135.3, 143.9, 149.7 ppm; IR (KBr)  $\tilde{v} = 3437$ (m), 2952 (s), 2924 (m), 1608 (m), 1486 (m), 1398 (m), 1361 (s), 1247 (s), 1248 (s), 1145 (m), 1091 (s), 860 (s), 837 (s), 751 cm<sup>-1</sup> (w); UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 271 nm (36961 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: m/z calcd for C<sub>46</sub>H<sub>67</sub>BO<sub>2</sub>S<sub>3</sub>Si<sub>3</sub>Na: 865.3365 [*M*+Na]<sup>+</sup>; found: 865.3076; elemental analysis calcd (%) for C<sub>46</sub>H<sub>67</sub>BO<sub>2</sub>S<sub>3</sub>Si<sub>3</sub> (842.37): C 65.52, H 8.01; found: C 65.74, H 8.06.

# 1-lodo-4-(tris{4-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)benzene (9)

A 50 mL, two-necked, round-bottomed flask was charged with pinacol ester 8 (0.15 g, 0.18 mmol), copper iodide (0.051 g, 0.27 mmol), N-iodosuccinimide (0.06 g, 0.27 mmol), anhydrous DMF (8 mL), and toluene (4 mL) under argon. The reaction mixture was stirred and heated at 110°C for 24 h under an argon atmosphere. After cooling, the reaction mixture was diluted with dichloromethane (200 mL) and washed with Na<sub>2</sub>SO<sub>3</sub> solution (10%, 100 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. All volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (100 g) with hexane/EtOAc (10:1) to obtain 0.14 g of **9** as a yellow powder in 91% yield.  $R_{\rm f} =$ 0.92 (hexane/EtOAc = 9:1); m.p. 70-71 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.04$  (s, 27 H), 0.92–0.95 (m, 6 H), 2.93–2.96 (m, 6 H), 6.92-6.93 (d, J=9 Hz, 2 H), 7.04-7.06 (m, 6 H), 7.14-7.16 (m, 6 H), 7.55–7.57 ppm (d, J=8 Hz 2H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta =$ -1.5, 16.9, 29.2, 63.8, 92.1, 127.4, 131.5, 131.6, 133.2, 135.7, 136.9, 143.4, 146.5 ppm; IR (KBr)  $\tilde{v} = 2952$  (s), 2923 (s), 2853 (w), 1590 (w), 1484 (w), 1399 (w), 1248 (s), 1006 (m), 858 (s), 809 (s), 753 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\varepsilon$ ) = 271 nm (38610 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI (+) HRMS: m/z calcd for  $C_{40}H_{55}IS_3Si_3Na$ : 865.1711 [*M*+Na]<sup>+</sup>; found: 865.1716; elemental analysis calcd (%) for  $C_{40}H_{55}IS_3Si_3$  (842.18): C 56.98, H 6.57; found: C 57.09, H 6.65.

#### S,S',S''-{4,4',4''-[(4-lodophenyl)methanetriyl)]tris(benzene-4,1diyl)} tris(thioacetate) (10)

The desired product was prepared according to the method described for the preparation of 7, starting from 9 (0.11 g, 0.13 mmol) and AgBF<sub>4</sub> (0.2 g, 1.05 mmol) in a mixture of dry dichloromethane (12 mL) and acetyl chloride (1.2 mL) under argon. The suspension was stirred at room temperature for 12 h. The crude product was purified by column chromatography on silica gel (150 g) in hexane/EtOAc (5:1) to provide 0.076 g of 10 as a white powder in 87% yield.  $R_f = 0.41$  (hexane/EtOAc = 3:1); m.p. 272–273 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.42$  (s, 9H), 6.95–6.97 (d, J = 9.5 Hz 2H), 7.22-7.24 (m, 6H), 7.30-7.32 (m, 6H), 7.58-7.60 ppm (d, J=8 Hz, 2 H); <sup>13</sup> C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$  = 30.5, 64.6, 92.7, 126.4, 131.8, 131.9, 133.1, 133.9, 137.2, 145.5, 146.9, 194.0 ppm; IR (KBr)  $\tilde{v} = 2924$ (s), 2854 (w), 1706 (s), 1485 (m), 1467 (w), 1390 (w), 1261 (m), 1092 (m), 817 (m), 616 cm<sup>-1</sup> (s); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\epsilon$ ) = 251 nm (18696 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: m/z calcd for  $C_{31}H_{25}IO_3S_3Na$ : 690.9903 [*M*+Na]<sup>+</sup>; found: 690.9890; elemental analysis calcd (%) for C<sub>40</sub>H<sub>55</sub>IS<sub>3</sub>Si<sub>3</sub> (668.00): C 55.69, H 3.77; found: C 55.52, H 3.68.

#### Tris{3-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methanol (13)

*Method A*: The desired product was prepared according to the method described for the preparation of **3**, starting from **11** (3 g, 10.4 mol) in anhydrous THF (30 mL), *tert*-BuLi (14 mL, 21 mmol, 15% in pentane), and diethyl carbonate (0.36 mL, 2.97 mmol) in anhydrous THF (6 mL) under argon. After 16 h, the reaction mixture was quenched, and the crude product was purified by column chromatography on silica gel (350 g) with hexane/EtOAc (9:1) to obtain 0.85 g of **13** as yellow oil in 44% yield and 0.52 g of **12** as a yellowish solid in 39% yield.

For **13**:  $R_f = 0.43$  (hexane/EtOAc = 9:1); m.p. 92–94 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.01$  (s, 27 H), 0.85–0.89 (m, 6H), 2.75 (s, OH), 2.86–2.89 (m, 6H), 7.01–7.03 (m, 3 H), 7.19–7.20 (m, 5 H); 7.20–7.23 ppm (m, 5 H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.6$ , 16.9, 29.4, 81.9, 125.4, 127.6, 127.9, 128.6, 137.5, 147.2 ppm; IR (KBr)  $\ddot{v} = 3460$  (m), 2950 (s), 1584 (m), 1467 (m), 1411 (m), 1247 (s), 846 (s), 695 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\varepsilon$ ) = 257 nm (25970 mol<sup>-1</sup>dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C<sub>34</sub>H<sub>52</sub>OS<sub>3</sub>Si<sub>3</sub>Na: 679.2380 [*M*+Na]<sup>+</sup>; found: 697.2307; elemental analysis calcd (%) for C<sub>34</sub>H<sub>52</sub>OS<sub>3</sub>Si<sub>3</sub> (656.25): C 62.14, H 7.98; found: C 62.29, H 8.08.

For **12**:  $R_{\rm f}$ =0.5 (hexane/EtOAc=9:1); m.p. 123-125 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =0.04 (s, 18H), 0.93-0.96 (m, 4H), 2.97-3.01 (m, 4H), 7.36-7.39 (m, 2H), 7.49-7.50 (m, 2H), 7.52-7.54 (m, 2H), 7.69 (s, 2H), 7.70 ppm (s, 1H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$ = -1.6, 16.9, 29.4, 128.8, 129.5, 132.5, 138.2, 138.6, 196.1 ppm; IR (KBr)  $\bar{\nu}$ =3055 (w), 2951 (s), 1658 (s), 1561 (s), 1431 (m), 1414 (m), 1260 (s), 847 (s), 695 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\rm max}$  ( $\varepsilon$ )=265 nm (23085 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) HRMS: *m/z* calcd for C<sub>23</sub>H<sub>34</sub>OS<sub>2</sub>Si<sub>2</sub>K: 485.1221 [*M*+K]<sup>+</sup>; found: 485.1247; elemental analysis calcd (%) for C<sub>23</sub>H<sub>34</sub>OS<sub>2</sub>Si<sub>2</sub> (446.16): C 61.83, H 7.67; found: C 61.67, H 7.90.

*Method B*: The desired product was prepared according to the method described for the preparation of **3**, starting from **11** (0.97 g, 3.35 mmol) in anhydrous THF (15 mL), *tert*-BuLi (4.55 mL, 6.71 mmol, 15% in pentane), and **12** (0.75 g, 1.6 mmol) in anhydrous THF (10 mL) under argon. After 12 h, the reaction mixture was quenched, and the crude product was purified by column chromatography on silica gel (200 g) in hexane/EtOAc (9:1) to yield 1 g (76%) of **13** as a yellowish oil.

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#### Bis(3-bromophenyl)methanone (15)

A flame-dried, argon-flushed 100 mL Schlenk flask was charged with 1,3-dibromobenzene (2 g, 8.47 mmol) and anhydrous THF (30 mL). The solution was cooled to  $-78\,^\circ\text{C}$  and *n*BuLi (1.6  $\,\text{m}$  in hexane, 5.3 mL, 8.48 mmol) was added dropwise over 20 min. The reaction mixture was stirred at -78°C for 2 h under argon. In a second 100 mL Schlenk flask, diethyl carbonate (0.21 mL, 1.7 mmol) was diluted in anhydrous THF (10 mL) under an inert atmosphere and cooled to -78 °C. The solution of lithiated species was added slowly through a cannula into the flask containing the carbonate solution. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 15 h. The reaction mixture was guenched with saturated NH<sub>4</sub>Cl solution (100 mL). The aqueous layer was washed with  $CH_2Cl_2$  (3×100 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO4, and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (200 g) in hexane/EtOAc (20:1) to afford 0.53 g of 15 as a white solid in 93% yield.  $R_f = 0.4$  (hexane/EtOAc = 20:1); m.p. 123–125 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.38–7.41 (m, 2H), 7.68-7.69 (m, 2H), 7.75-7.77 (m, 2H), 7.91-7.92 ppm (m, 2 H); <sup>13</sup>C NMR (125.8 MHz,  $CD_2CI_2$ ):  $\delta = 123.0$ , 128.9, 130.5, 133.0, 136.0, 139.3, 193.8 ppm; IR (KBr)  $\tilde{v} = 3061$  (w), 2922 (m), 1651 (s), 1563 (s), 1470 (m), 1417 cm $^{-1}$  (m); UV/Vis (CH $_2$ Cl $_2$ ):  $\lambda_{max}$  ( $\epsilon$ ) = 265 nm (9490 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) HRMS: m/z calcd for C<sub>13</sub>H<sub>8</sub>Br<sub>2</sub>ONa: 362.8814 [*M*+Na]<sup>+</sup>; found: 362.8802; elemental analysis calcd (%) for C<sub>13</sub>H<sub>8</sub>Br<sub>2</sub>O (337.89): C 45.92, H 2.37; found: C 45.97, H 2.34.

#### Tris(3-bromophenyl)methanol (16)

In a 100 mL Schlenk flask, 1,3-dibromobenzene (1.9 g, 8.1 mmol) was dissolved in anhydrous THF (30 mL) under argon, cooled to -78°C, and degassed. Then, nBuLi (1.6м in hexane, 5.3 mL, 8.4 mmol) was added dropwise over 20 min, and the resulting mixture was stirred at -78°C for 2 h. In a second 100 mL Schlenk flask, 15 (1.8 g, 5.33 mmol) was dissolved in THF (10 mL) under argon, and cooled to -78 °C. The solution of lithiated species was added slowly through a cannula into the flask containing the solution of 15. The yellow solution was stirred at -78 °C for 2 h, then allowed to warm to room temperature and stirred for an additional 12 h. The reaction mixture was quenched with saturated NH<sub>4</sub>Cl solution (100 mL). The aqueous layer was washed with  $CH_2CI_2$  (3× 100 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography (300 g) in hexane/EtOAc (10:1) to provide 2.15 g of **16** as a yellow oil in 82% yield.  $R_f = 0.29$  (hexane/EtOAc = 10:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.07 (s, OH), 7.13–7.14 (d, J = 7.9 Hz, 3 H), 7.19-7.22 (m, 3 H), 7.44-7.46 (d, J=7.85 Hz, 3 H), 7.48 ppm (s, 3 H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 68.1$ , 122.9, 126.8, 130.0, 130.8, 131.2, 148.1 ppm; IR (KBr)  $\tilde{v} = 3442$  (s), 3061 (m), 2926 (s), 1564 (s), 1470 (s), 1416 (m), 1416 (m), 1200 (m),  $785 \text{ cm}^{-1}$ UV/Vis  $(CH_2CI_2)$ : (w);  $\lambda_{\max}$  $(\varepsilon) = 267 \text{ nm}$  $(5540 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ ; ESI(+) HRMS: m/z calcd for C<sub>19</sub>H<sub>13</sub>Br<sub>3</sub>ONa: 518.8389 [*M*+Na]<sup>+</sup>; found: 518.8376; elemental analysis calcd (%) for C<sub>19</sub>H<sub>13</sub>Br<sub>3</sub>O (493.25): C 45.92, H 2.64; found: C 45.99, H 2.56.

#### 4-[Tris(3-bromophenyl)methyl]phenol (17)

The desired product was prepared according to the method described for the preparation of **4**, starting from **16** (2.13 g, 4.32 mmol), phenol (4.81 g, 51 mmol), and a few drops of concentrated HCl. The reaction mixture was heated at 120 °C for 14 h

under argon. The residue was purified by column chromatography on silica gel (300 g) in hexane/EtOAc (10:1) to afford 2.17 g of **17** as a white solid in 88% yield.  $R_f$ =0.35 (hexane/EtOAc=10:1); m.p. 178–180 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =5.17 (s, OH), 6.75–6.76 (d, *J*=8.8 Hz, 2H), 6.97–6.99 (d, *J*=8.8 Hz, 2H), 7.06–7.07 (d, *J*= 8.05 Hz, 3H), 7.13–7.16 (m, 3H), 7.32 (s, 3H), 7.35–7.37 ppm (d, *J*= 9.25 Hz, 3H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$ =64.1, 115.1, 122.4, 129.5, 129.9, 130.0, 132.3, 133.5, 137.3, 148.4, 154.3 ppm; IR (KBr)  $\bar{v}$ =3422 (s), 3058 (m), 2922 (m), 1590 (s), 1468 (m), 1404 (m), 1215 (m), 832 (s), 782 cm<sup>-1</sup> (s); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ )=280 nm (4420 mol<sup>-1</sup>dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) HRMS: *m/z* calcd for C<sub>25</sub>H<sub>17</sub>Br<sub>3</sub>ONa: 594.8682 [*M*+Na]<sup>+</sup>; found: 596.8680; elemental analysis calcd (%) for C<sub>25</sub>H<sub>17</sub>Br<sub>3</sub>O (569.88): C 52.39, H 2.99; found: C 52.42, H 2.88.

#### Trimethyl{4-[tris(3-bromophenyl)methyl]phenoxy}silane (18)

Trimethylsilyl chloride (0.50 g, 4.17 mmol) was added dropwise to a solution of 17 (1.32 g, 2.32 mmol) in a mixture of anhydrous triethylamine (0.43 g, 4.17 mmol) and diethyl ether (11 mL) at -78 °C under an argon atmosphere. The reaction mixture was stirred for 3 h, then allowed to warm to room temperature and stirred for an additional 12 h. The resulting solution was quenched with water (100 mL). The aqueous layer was washed with  $CH_2CI_2$  (2×150 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub>, and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (130 g) with hexane/EtOAc (9:1) to obtain 1.32 g of 18 as a white powder in 89% yield.  $R_{\rm f}$  = 0.84 (hexane/ EtOAc = 9:1); m.p. 42-45 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.28 (s, 9H), 6.75-6.77 (d, J=8.8 Hz, 2H), 6.96-6.98 (d, J=8.8 Hz, 2H), 7.07-7.08 (d, J=8.05 Hz, 3 H), 7.13-7.17 (m, 3 H), 7.32 (s, 3 H), 7.36-7.37 ppm (d, J=7.8 Hz, 3 H);  $^{13}\mathrm{C}$  NMR (125.8 MHz, CDCl\_3):  $\delta\!=\!0.5,$ 64.1, 119.4, 122.3, 129.4, 129.8, 130.0, 132.1, 133.6, 137.7, 148.4, 153.9 ppm; IR (KBr)  $\tilde{v}$  = 3034 (m), 2956 (m), 1585 (s), 1470 (m), 1406 (m), 1215 (m), 832 (s), 782 cm<sup>-1</sup> (s); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 274 nm (9059 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) HRMS: m/z calcd for C<sub>25</sub>H<sub>17</sub>Br<sub>3</sub>ONa: 596.8682 [*M*+Na, -TMS]<sup>+</sup>; found: 594.8690; elemental analysis calcd (%) for  $C_{28}H_{25}Br_3OSi$  (641.92): C 52.12, H 3.91; found: C 52.34, H 3.97.

#### 4-(Tris{3-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)phenol (14)

A 25 mL pressure tube was charged with 18 (1.3 g, 2.03 mmol), Xantphos (0.094 g, 0.016 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.093 g, 0.0089 mmol), and anhydrous dioxane (14 mL). The tube was evacuated and refilled with argon three times. Then N,N-diisopropylethylamine (2.3 g, 18 mmol) and 2-(trimethylsilyl)ethanethiol (2.5 g, 12 mmol) were added under argon and the tube was sealed quickly. The reaction mixture was heated at 120 °C for 24 h, then cooled, diluted with dichloromethane (200 mL), and washed with a solution of HCl (1 м, 100 mL). The combined organic layer was washed with brine (100 mL), dried over MgSO4, and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (300 g) in hexane/EtOAc (10:1) to provide the title compound 14 (1.36 g) as a yellow oil in 92% yield.  $R_f = 0.2$  (hexane/EtOAc = 10:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = -0.02$  (s, 27 H), 0.80–0.84 (m, 6 H), 2.77–2.81 (m,6 H), 5.04 (s, OH), 6.69–6.71 (d, J=8.75 Hz, 2 H), 6.95–6.99 (d, J=8.54 Hz, 3 H), 7.02-7.03 (d, J=8.75 Hz, 2 H), 7.11-7.12 (m, 6 H), 7.13-7.17 ppm (m, 3 H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.6$ , 16.9, 29.5, 68.2, 114.6, 126.6, 128.1, 128.8, 131.2, 132.5, 136.7, 138.4, 147.4, 154.0 ppm; IR (KBr):  $\tilde{v} = 3435$  (s), 3055 (m), 2951 (s), 1582 (m), 1509 (m), 1471 (m), 1430 (m), 1248 (s), 857 (s), 840 (s), 687  $\rm cm^{-1}$  (w); UV/



Vis  $(CH_2CI_2)$ :  $\lambda_{max}$  ( $\epsilon$ ) = 275 nm (51292 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C<sub>40</sub>H<sub>56</sub>OS<sub>3</sub>Si<sub>3</sub>Na: 755.2693 [*M*+Na]<sup>+</sup>; found: 755.2515; elemental analysis calcd (%) for C<sub>40</sub>H<sub>56</sub>OS<sub>3</sub>Si<sub>3</sub> (732.28): C 65.52, H 7.70; found: C 66.15, H 7.81.

#### 4-(Tris{3-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)phenyl trifluoromethanesulfonate (19)

The desired product was prepared according to the method described for the preparation of 5, starting from 14 (0.3 g, 0.41 mmol), triflic anhydride (0.2 g, 0.71 mmol) in a mixture of anhydrous triethylamine (0.12 mL, 0.82 mmol) and dichloromethane (25 mL) at -78 °C under argon. The reaction mixture was stirred for 6 h, then allowed to warm to room temperature and stirred for an additional 10 h. The residue was purified by column chromatography on silica gel (150 g) in hexane/EtOAc (9:1) to provide to the title compound **19** (0.29 g) as a yellowish oil in 83% yield.  $R_f = 0.81$ (hexane/EtOAc = 9:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.01 (s, 27 H), 0.81-0.84 (m, 6H), 2.78-2.82 (m, 6H), 6.92-6.93 (m, 3H), 7.07-7.08 (m, 3H), 7.13-7.17 (m, 6H), 7.17-7.20 (m, 2H), 7.28-7.30 ppm (d, J=3 Hz, 2H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.6$ , 17.2, 29.7., 65.2, 120.9, 127.0, 128.7, 128.8, 131.2, 133.4, 137.9, 146.9, 147.3, 148.3 ppm;  $^{\rm 19}$  F NMR (470.57 MHz, CDCl\_3):  $\delta\!=\!-73.30$  ppm; IR (KBr):  $\tilde{v} = 3060$  (w), 2953 (m), 1582 (m), 1497 (w), 1427 (m), 1250 (s), 1213 (s), 1142 (s), 840 (s), 785 (w), 697 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  $(\varepsilon) = 268 \text{ nm} (25170 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}); \text{ ESI}(+) \text{ MS: } m/z \text{ calcd for}$ C<sub>41</sub>H<sub>55</sub>O<sub>3</sub>S<sub>4</sub>FSi<sub>3</sub>Na: 887.2186 [*M*+Na]<sup>+</sup>; found 887.2126; elemental analysis calcd (%) for  $C_{41}H_{55}O_3S_4Si_3F$  (864.23): C 56.91, H 6.41; found: C 57.03, H 6.59.

#### 4-(Tris{3-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)benzonitrile (20)

The desired product was prepared according to the method described for the preparation of 6, starting from triflate 19 (0.15 g, 0.17 mmol), zinc cyanide (0.049 g, 0.42 mmol), copper(l) cyanide (0.015 g, 0.17 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.029 g, 0.025 mmol) in anhydrous DMF (10 mL) under argon. After 16 h at 140  $^\circ\text{C},$  the reaction mixture was purified by column chromatography on silica gel (100 g) in a mixture of hexane/EtOAc (9:1) to provide 0.13 g of 20 as a yellow oil in 74% yield.  $R_f = 0.67$  (hexane/EtOAc = 9:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = -0.01$  (s, 27 H), 0.80–0.84 (m, 6 H), 2.78–2.81 (m, 6H), 6.91–6.93 (d, J=10.5 Hz, 3H), 7.07 (s, 3H), 7.13–7.15 (d, J= 7.8 Hz,2 H), 7.17-7.20 (m, 3 H), 7.34-7.36 (d, J=8.55 Hz, 2 H), 7.54-7.56 ppm (d, J = 8.6 Hz, 2H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta =$ -1.57, 16.84, 29.45, 65.29, 110.39, 118.87, 126.79, 128.43, 128.47, 130.83, 131.65, 131.87, 137.49, 154.96, 151.72 ppm; IR (KBr):  $\tilde{v} = 262$ (17540), 3059 (s), 2951 (s), 2228 (m), 1582 (s), 1471 (m), 1407 (m), 1248 (m), 1161 (s), 875 (s), 860 (s), 696  $\rm cm^{-1}$  (w); UV/Vis (CH\_3CN):  $\lambda_{max}$  ( $\varepsilon$ ) = 224 nm (19670 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: *m/z* calcd for C<sub>41</sub>H<sub>55</sub>S<sub>3</sub>Si<sub>3</sub>K: 780.2436 [*M*+K]<sup>+</sup>; found: 780.2485; elemental analysis calcd (%) for C<sub>41</sub>H<sub>55</sub>OS<sub>3</sub>Si<sub>3</sub> (741.28): C 66.34, H 7.47, N 1.89; found: C 66.49, H 7.65, N 1.91.

#### S,S',S''-{3,3',3''-[(4-Cyanophenyl)methanetriyl)]tris(benzene-4,1-diyl)} tris(thioacetate) (21)

The desired product was prepared according to the method described for **7**, starting from **20** (0.12 g, 0.16 mmol), AgBF<sub>4</sub> (0.22 g, 1.12 mmol), and acetyl chloride (1.2 mL) in anhydrous dichloromethane (12 mL) under argon. After 12 h at room temperature, the reaction mixture was quenched and purified by column chromatography on silica gel (150 g) in hexane/EtOAc (3:1) to give 0.07 g of **21** as an orange powder in 77% yield.  $R_{\rm f}$ =0.11 (hexane/EtOAc =

3:1); m.p. 151–154 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.35 (s. 9H), 7.26 (s, 3H), 7.28–7.30 (d-d, *J*=4.25 Hz, 3H), 7.35–7.38 (m, 6H), 7.43–7.45 (d, *J*=8.35 Hz 2H), 7.59–7.61 ppm (d, *J*=8.4 Hz, 2H); <sup>13</sup> C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$ =30.4, 65.1, 110.6, 118.8, 128.2, 129.1, 131.6, 131.8, 132.0, 132.7, 137.2, 146.1, 151.0, 193.7 ppm; IR (KBr):  $\bar{v}$ =3060 (s), 2923 (s), 2228 (s), 1705 (s), 1584 (m), 1470 (s), 1408 (m), 1416 (m), 1243 (m), 1118 (s), 613 cm<sup>-1</sup> (s); UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$ ( $\varepsilon$ ) = 223 nm (48219 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) HRMS: *m/z* calcd for C<sub>32</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>3</sub>Na: 590.0889 [*M*+Na]<sup>+</sup>; found: 590.0872; elemental analysis calcd (%) for C<sub>32</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>3</sub> (567.10): C 67.70, H 4.44, N 2.47; found: C 67.82, H 4.49, N 2.52.

#### 4-(Tris{3-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)phenylboronic acid pinacol ester (22)

The desired product was prepared according to the method described for 8, starting from triflate 19 (0.29 g, 0.34 mmol), anhydrous potassium acetate (0.14 g, 1.36 mmol), bis(pinacolato)diboron (0.13 g, 0.51 mmol), and Pd(dppf)Cl<sub>2</sub> (0.028 g, 0.034 mmol) in anhydrous dioxane (15 mL) under argon. After 16 h at 120°C, the residue was purified by column chromatography on silica gel (130 g) in hexane/EtOAc (10:1) to provide 0.23 g of 22 as a yellow powder in 82% yield. R<sub>f</sub>=0.48 (hexane/EtOAc=10:1); m.p. 129-130 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = -0.02$  (s, 27 H), 0.79–0.83 (m, 6H), 1.32 (s, 12H), 2.76-2.80 (m, 6H), 6.97-6.99 (m, 3H), 7.10-7.11 (m, 3H), 7.13-7.16 (m, 6H), 7.21-7.22 (d, J=8.25 Hz, 2H), 7.67-7.69 ppm (d, J = 8.4 Hz 2 H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = -1.6$ ; 16.9, 25.1, 29.5, 65.3, 83.9, 126.6, 127.8, 128.1, 128.7, 130.6, 131.2, 134.3, 136.8, 147.0, 149.3 ppm; IR (KBr): v=3059 (s), 2950 (s), 2921 (s), 2852 (w), 1733 (m), 1609 (m), 1580 (s), 1470 (w), 1427 (m), 1364 (s), 1247 (s), 1213 (s), 1143 (s), 1091 (m), 860 (s), 838 (s), 704 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 265 nm (27425 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: m/z calcd for  $C_{46}H_{67}BO_2S_3Si_3Na$ : 865.3605  $[M+Na]^+$ ; found: 865.3226; elemental analysis calcd (%) for C46H67BO2S3Si3 (842.37): C 65.52, H 8.01; found: C 65.73, H 8.12.

#### 1-lodo-4-(tris{3-[2-(trimethylsilyl)ethylsulfanyl]phenyl}methyl)benzene (23)

The desired product was prepared according to the method described for 9, starting from pinacol ester 22 (0.36 g, 0.43 mmol), copper iodide (0.12 g, 0.64 mmol), and N-lodosuccinimide (0.14 g, 0.64 mmol) in anhydrous DMF (13 mL) and toluene (6.5 mL) under argon. After 24 h at 110 °C, the residue was purified by column chromatography on silica gel (120 g) in hexane/EtOAc (10:1) to give 0.3 g of 23 as a yellow powder in 83% yield.  $R_{\rm f}$ =0.75 (hexane/EtOAc = 10:1); m.p. 136–137 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta\,{=}\,{-}0.0$  (s, 27 H), 0.81–0.85 (m, 6 H), 2.80–2.84 (m, 6 H), 6.98–7.00 (m, 5H), 7.11-7.14 (m, 6H), 7.17-7.20 (m, 3H), 7.59-7.61 ppm (d, J = 7.8 Hz, 2 H); <sup>13</sup>C NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -1.55$ , 17.27, 29.73, 65.27, 92.49, 126.86, 128.66, 128.72, 131.13, 133.55, 137.33, 137.77, 146.63; 147.1 ppm; IR (KBr):  $\tilde{v} = 3058$  (s), 2952 (s), 2921 (s), 2853 (w), 1581 (s), 1473 (w), 1248 (s), 1006 (m), 840 (s), 728 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 267 nm (24704 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); ESI(+) MS: m/z calcd for C<sub>40</sub>H<sub>55</sub>S<sub>3</sub>ISi<sub>3</sub>Na: 865.1711 [*M*+Na]<sup>+</sup>; found: 887.1564; elemental analysis calcd (%) for  $C_{40}H_{55}IS_3Si_3$  (842.18): C 56.98, H 6.57; found: C 57.11, H 6.70.

#### S,S',S"-{3,3',3"-[(4-lodophenyl)methanetriyl)]tris(benzene-4,1diyl)} tris(thioacetate) (24)

The desired product was prepared according to the method described for **7**, starting from **23** (0.29 g, 0.43 mmol), with  $AgBF_4$  (0.4 g, 2.06 mmol) in a mixture of anhydrous dichloromethane

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(18 mL) and acetyl chloride (1.8 mL) under argon. The suspension was stirred at room temperature for 12 h. The crude product was purified by column chromatography on silica gel (150 g) in hexane/EtOAc (5:1) to provide 0.2 g of **24** as a yellow powder in 55% yield.  $R_f$ =0.31 (hexane/EtOAc=5:1); m.p. 122–125°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =2.37 (s. 9H), 7.02–7.05 (d, *J*=8.6 Hz 3 H), 7.26–7.27 (m, 6H), 7.27–7.29 (m, 3 H), 7.32–7.35 (m,3H), 7.61–7.62 ppm (d, *J*=8.6 Hz, 2 H); <sup>13</sup> C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$ =30.4, 64.7, 92.7, 127.9, 129.0, 131.8, 132.6, 133.1, 137.2, 137.3, 145.5, 146.7, 193.9 ppm; IR (KBr):  $\tilde{v}$ =3056 (s), 2924 (s), 2853 (w), 1702 (s), 1583 (m), 1467 (m), 1402 (m), 1119 (s), 947 (m), 613 cm<sup>-1</sup> (s); UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$ )=209 nm (39207 mol<sup>-1</sup>dm<sup>3</sup> cm<sup>-1</sup>); ESI (+) HRMS: *m/z* calcd for C<sub>31</sub>H<sub>25</sub>IO<sub>3</sub>S<sub>3</sub> (668.00): C 55.69, H 3.77; found: C 55.58, H 3.72.

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