

Preparation of Dendritic Multisulfides and Their Assembly on Air/Water Interfaces and Gold Surfaces

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Poly(propylene imine) (PPI) dendrimers of generations 1–5 have been derivatized with dialkyl sulfide chains. On water, these dendrimers form stable LB films with densely packed alkyl chains pointing to the air and cores exposed to the aqueous solution. Self-assembly of the same dendrimers from solution onto a gold surface leads to a flattened orientation of the molecules on the surface, as shown by high contact angle hystereses, high electrochemical capacitances, and low charge transfer resistances. X-ray photoelectron spectroscopy data indicate that the formation of the flattened structure can be attributed to adsorption to the gold surface of not only part of the sulfide moieties in the alkyl chains, but also part of the tertiary amines in the core. The electrochemically determined surface coverages of ferrocene-modified dendritic wedges (with similar molecular structures as those of the dialkyl sulfide PPI dendrimers) confirm the proposed flattened, surface-spread dendritic structure. In contrast, LB films of the sulfide PPI dendrimers that were transferred onto gold appear to largely remain their original, densely packed state, as for these films smaller contact angle hystereses and higher charge transfer resistances are measured than those observed for the monolayers prepared by self-assembly from solution. Additionally, the electrochemical capacitances of the transferred LB films point to a layer thickness comparable to the thickness of a densely packed didecylsulfide monolayer. The results in this study demonstrate that different surface architectures can be prepared of the same compounds by solely varying the preparation procedure.

Introduction

Self-assembled monolayers (SAMs) and Langmuir–Blodgett (LB) films are highly ordered supramolecular systems that are able to modify macroscopic properties of interfaces. On the basis of a breakthrough in surface analysis, these supramolecular arrangements have been intensively investigated in the last two decades.¹ The ability to control chemical and structural properties of interfaces is becoming increasingly important in electronics, sensing, catalysis, biomedics, and many other fields. Therefore, more and more complex systems are designed for specific applications.

Attractive macromolecular systems for surface modification are dendritic polymers,² because these polymers are defined in shape, are essentially monodisperse and contain a distinct number of (end-)functionalities, enabling their use as supramolecular building blocks. Different approaches have been followed to fabricate highly ordered adsorbate layers of dendritic polymers,^{3–5} and, for example, applications as resists for scanning probe lithography⁶

and as adhesion promoters between glass and vapor-deposited gold⁷ have already been demonstrated.

Dialkyl sulfide derivatives have been used before by us in order to prepare densely packed, well-ordered monolayers on gold.⁸ Some of these monolayers⁹ appear to be of such high quality that they block etching of the underlying gold by ferro/ferricyanide when applied in a lithographic pattern replication technique called micro-contact printing.¹⁰

In this report we have systematically studied the assembly of modified poly(propylene imine) (PPI) den-

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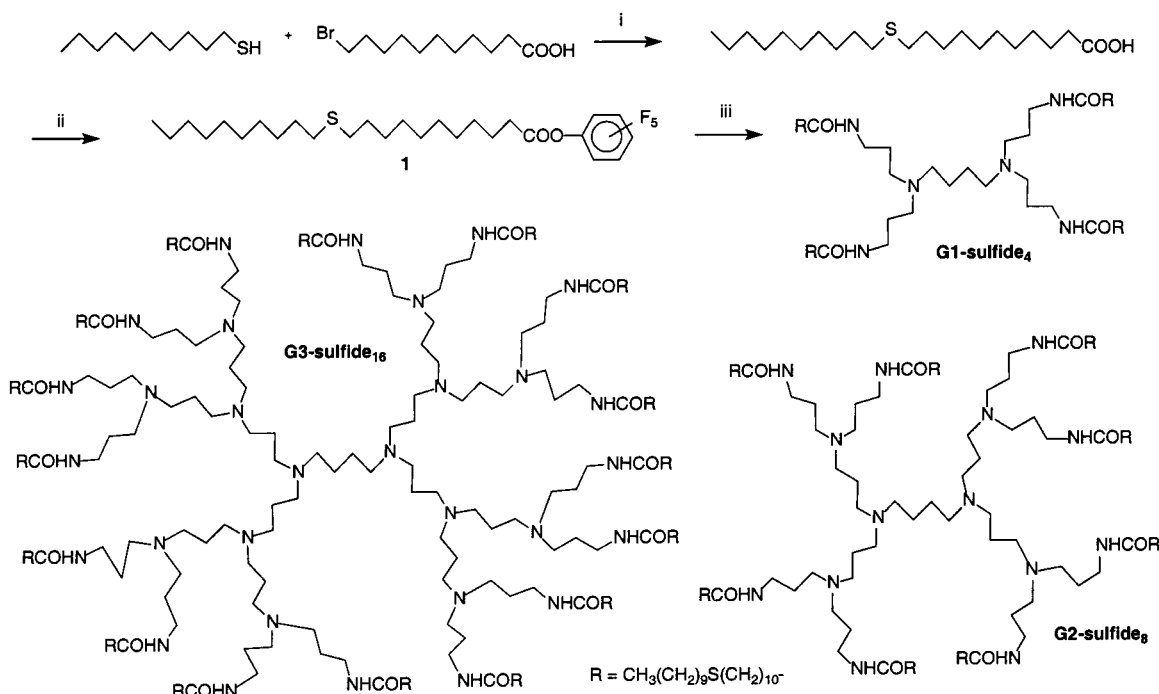
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Scheme 1. (i) KOH, EtOH, Reflux. (ii) DCC, C₆F₅OH, THF, Room Temperature. (iii) Amine-Terminated Dendrimer, CHCl₃, Room Temperature. G4-Sulfide₃₂ and G5-Sulfide₆₄ Were Also Prepared



dendrimers at gold and air/water surfaces. The PPI dendrimers have been decorated with dialkyl sulfide chains to create building blocks that can order on water surfaces due to their amphiphilicity and that can self-assemble on gold due to their sulfide moieties.¹¹ Contact angle measurements, electrochemistry, XPS, and AFM have been used to monitor their adsorption on gold surfaces. Sulfide-modified dendritic wedges with a ferrocene headgroup were synthesized to specifically study the surface coverage of the dendrimers. Differences in architecture between surface layers prepared by self-assembly from solution and by transfer of LB films onto gold are discussed. The implications of these architectures for application in microcontact printing are briefly addressed.

Results and Discussion

Synthesis and Characterization. Poly(propylene imine) dendrimers of generation 1–5¹² were converted to sulfide modified dendrimers G1-sulfide₄, G2-sulfide₈, G3-sulfide₁₆, G4-sulfide₃₂, G5-sulfide₆₄, and G4-palm₂₆-sulfide₆ using the sequence of reactions shown in Scheme 1 for the second-generation dendrimer. First, 1-decanethiol was coupled with 11-bromoundecanoic acid in boiling EtOH using KOH as the base. After purification, the thioether-carboxylic acid product was reacted with pentafluorophenol using dicyclohexylcarbodiimide (DCC) as dehydrating agent to give **1**. The activated ester of palmitic acid (**2**, not shown in Scheme 1) was also prepared by a DCC coupling procedure. Modification of the dendrimers was achieved by overnight stirring of the dendrimer and the activated ester(s) of choice in CHCl₃. Purification of the

dendrimers consisted of a precipitation in hexane, washing of a dendrimer chloroform solution with basic water and a precipitation in MeOH.

The dendrimers were characterized by ¹H NMR and ¹³C NMR spectroscopy, elemental analysis, MALDI-TOF mass spectrometry and ATR-FTIR spectroscopy. The measured elemental contents of G1-sulfide₄ and G2-sulfide₈ are within the boundaries that are set for pure compounds, i.e., within 0.4% of calculated mass percentages. The carbon contents of the higher generations are somewhat too low, suggesting residual H₂O or MeOH in the dendritic interiors. The dendrimers up to generation 3 (the higher generations are too heavy) were analyzed with MALDI-TOF MS (see Figure 1). Apart from the expected isotope cluster of G1-sulfide₄ at 1678–1682 *m/z* and peaks around 800 *m/z* that are routinely observed when α -cyano cinnamic acid matrixes are used, clusters corresponding to Na⁺- (or possibly K⁺-) adducts and clusters corresponding to sulfoxide groups (and possibly sulfonyl groups¹³) are observed. The multiple oxidations of the dendrimers must have taken place in the laser desorption process, since NMR spectroscopy does not reveal resonances that can be assigned to CH₂S(O)CH₂ or CH₂S(O)₂CH₂ methylene groups. G2-sulfide₈ shows expected isotope clusters of H⁺-, Na⁺- and K⁺-adducts (not shown in Figure 1). Isotope clusters are not resolved for G3-sulfide₁₆; instead, broad peaks at ca. 6760, 6990, 7040 and 7160, *m/z* are observed (see Figure 1). The main peak corresponds to the fully functionalized material, whereas the minor peak at 6760 *m/z* corresponds to a dendrimer with 15 sulfide arms. The origin of the other two minor peaks is unknown to us. Dendrimer G4-palm₂₆-sulfide₆ has been characterized by NMR only, showing full conversion of all primary amine functionalities and the

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(13) It seems that only sulfoxides CH₂S(O)CH₂ and not sulfonyls CH₂S(O)₂CH₂ are formed, since the cluster sequence observed for G1-sulfide₈ stops at the clusters accounting for the quarterly oxidized starting dendrimer (at about *m/z* 1745) or its Na⁺-adduct (at about *m/z* 1768).

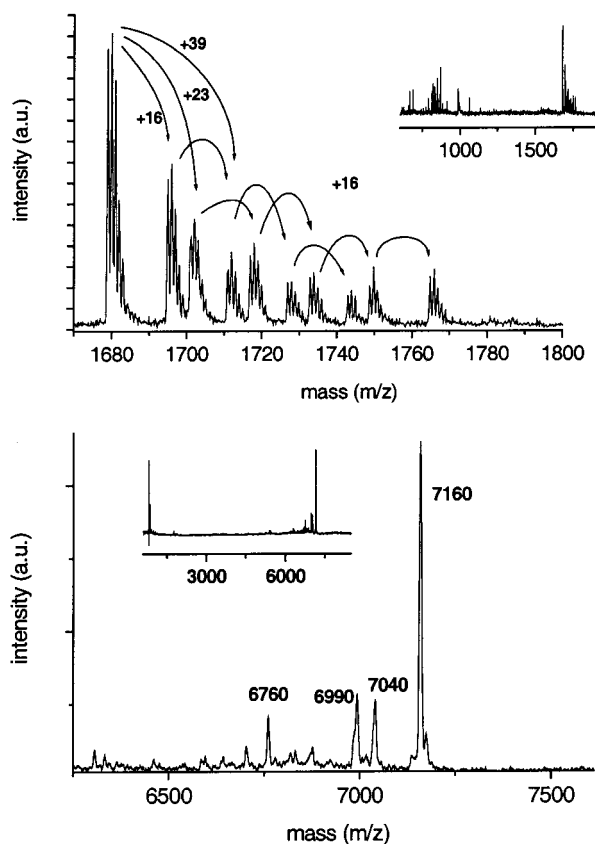
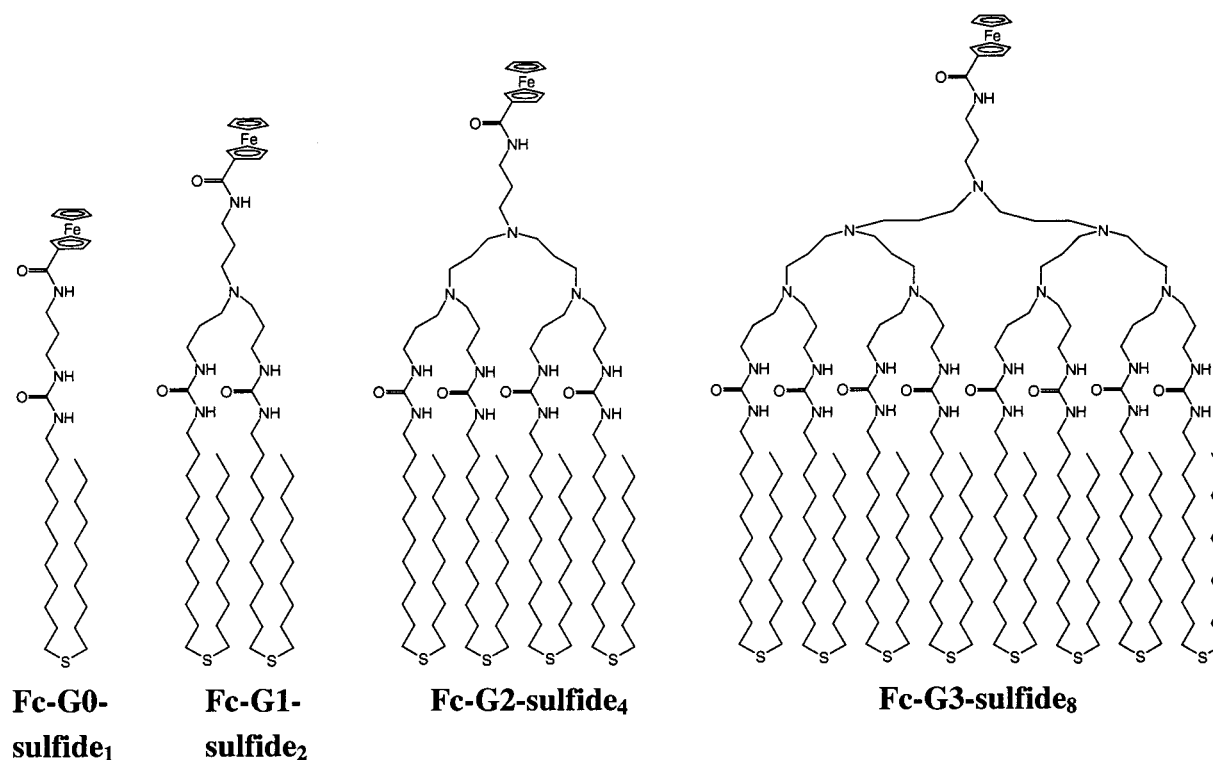
Scheme 2. Ferrocene-Modified, Sulfide-Terminated Poly(propylene imine) Dendritic Wedges

Figure 1. MALDI-TOF MS data on G1-sulfide₄ and G3-sulfide₁₆; the insets are the total recorded spectra, and details are shown in full.

presence of, on average, six sulfide chains per molecule, in accordance with the ratio of palmitoyl and sulfide building blocks used in the coupling reaction.

The sulfide-modified dendritic wedges with a ferrocene headgroup (Scheme 2) were prepared for generations 0–3 (1, 2, 4 or 8 sulfide moieties). Ferrocenecarboxylic acid was reacted with 1,3-diaminopropane to give Fc-G0-NH₂. The larger amine-terminated generations were prepared by stepwise reaction with acrylonitrile and subsequent reduction as is done for the preparation of the complete PPI dendrimers.¹² Sulfide chains were attached to the ferrocene wedges via urea linkages using an activated form of 11-aminoundecyldecylsulfide.

Langmuir–Blodgett Films. The sulfide poly(propylene imine) dendrimers have been tested on their ability to form monolayers on water by Langmuir–Blodgett techniques. The isotherms collected in Figure 2 show sharp increases of the pressure upon compression for all dendrimer generations, indicating the formation of stable monolayers. The pressures at which the monolayers start collapsing are in all cases slightly above 30 mN/m. For G2-sulfide₈, the monolayer was compressed to 25–30 mN/m (before collapse), expanded to the original zero-pressure state and compressed again. The second compression curve showed a sharp increase of pressure at the same area as observed in the first compression, again illustrating that these sulfide dendrimers form stable monolayers. The area occupied by one dendritic molecule as a function of the number of sulfide chains attached to this molecule is shown in the inset of Figure 2. The squares and circles correspond to, respectively, (i) the area per molecule just before collapse in the maximum compressed state and (ii) the area per molecule at the onset of the sharp pressure increase in the minimum compressed state. Linear relationships can clearly be seen, demonstrating that the series of dendrimers form similar type of monolayers, i.e., the amphiphilic dendritic molecules of different generations pack in a similar fashion within the monolayers. The tangents of the curve-fitted lines signify the area occupied per sulfide chain. Depending on the

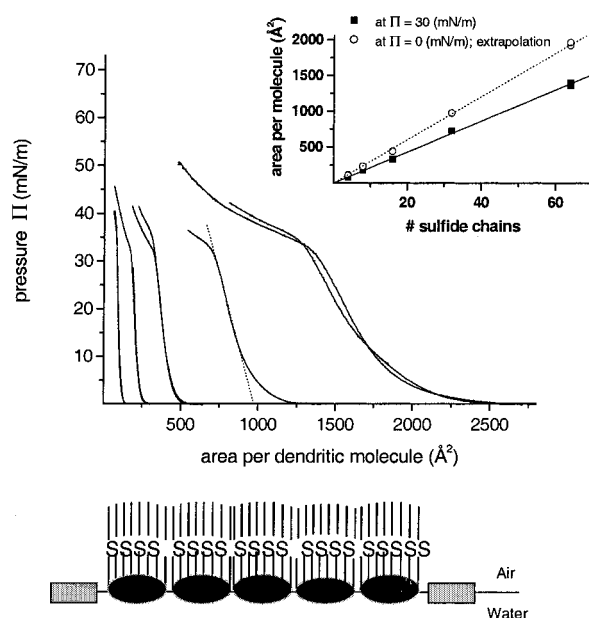


Figure 2. The main graph shows the Langmuir–Blodgett isotherms (20 °C) of five generations of sulfide dendrimers; generations 1, 2, 3, and 5 have been measured twice. The inset shows the occupied area per dendritic molecule as a function of the number of sulfide chains attached to the dendrimer: the solid squares indicate the areas at $\Pi = 30$ mN/m and the open circles indicate the areas at $\Pi = 0$. The latter values are obtained by extrapolation (see the fit for the fourth-generation dendrimer in the main graph). The cartoon below is a model for the compressed dendrimer monolayers.

degree of compression, this value varies between 22 $\text{\AA}^2$ (solid line) and 30 $\text{\AA}^2$ (dotted line).

Monolayers on water have already been reported for poly(propylene imine) dendrimers with palmitoyl or [4-(4-hexyloxyphenylazo)phenyloxy] undecanoyl chains.^{3c,d} The Π –A characteristics of monolayers of these dendrimers are similar to those observed for the sulfide dendrimers, although the two previously investigated dendritic monolayers are less susceptible to breakdown, as they have been found to be stable up to pressures of 55–65 mN/m. The areas per endgroup are comparable for all three investigated dendrimer systems: onsets of pressure increase have been observed at 25, 30, and 31 $\text{\AA}^2$, for the palmitoyl, sulfide, and [4-(4-hexyloxyphenylazo)phenyloxy] undecanoyl functionalized dendrimers, respectively. These values correspond quite well to those found for monolayers formed by alkylcarboxylates¹⁴ or alkylthiocarboxylic acids.¹⁵ On the bases of gathered data, a model for the packing of the sulfide dendrimers in the monolayers at the water–air interface can be made. The bottom graph of Figure 2 shows a cartoon of this model: the hydrophilic amine interiors of the dendrimers are facing the water layer, whereas the sulfide aliphatic chains are pointing upward to the air (this model has also been presented for the previously investigated palmitoyl and [4-(4-hexyloxyphenylazo)phenyloxy] undecanoyl substituted dendrimers^{3c}). Apparently, PPI dendrimers have no steric constraints hindering the formation of a “standing-up”-like building block as the one shown in Figure 2.

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Table 1. Advancing (θ_{ADV}) and Receding (θ_{REC}) Contact Angles of Water Droplets and Electrochemical Results on Gold Substrates Covered with Adsorbate Layers of Dendritic Systems

adsorbate	$\theta_{\text{ADV}}/\theta_{\text{REC}}$ (deg)	C_{ML} ($\mu\text{F}/\text{cm}^2$)	HET (μA)	R_{CT} (Ω)
G1-sulfide ₄	75°/15°	10.4	183	50
G3-sulfide ₁₆	70°/12°	n.d.	n.d.	n.d.
G5-sulfide ₆₄	71°/13°	9.3	173	56
G4-palm ₂₆ -sulfide ₆	91°/40°	11.0	103	209
G1-sulfide ₄ (LB film)	106°/64°	7.4	145	281
G5-sulfide ₆₄ (LB film)	110°/80°	6.6	130	203
didecylsulfide ^a	107°/86°	5.5	2	3000
Fc-G0-sulfide ₁	74°/14°	6.1		1500
Fc-G1-sulfide ₂	73°/11°	5.9		180
Fc-G2-sulfide ₄	73°/12°	5.5		150
Fc-G3-sulfide ₈	72°/12°	5.6		240

^a See ref 9.

Characterization of Adsorbate Layers on Gold.

Layers of G1-sulfide₄, G3-sulfide₁₆, and G5-sulfide₆₄ on gold were prepared by two different methods: (i) self-assembly from solution by immersion of gold substrates in 0.1 mM solutions of the dendrimers in ethanol/chloroform 1:2 for 12 h and (ii) transfer of LB monolayers from the air–water interface. The multisulfide adsorbate films were studied by contact angle goniometry and by electrochemical measurements, and the properties of the layers were compared with each other and with those of well-studied SAMs of didecylsulfide on gold.⁹ After self-assembly, didecylsulfide—a molecule with just one sulfide unit—fully covers a gold surface and forms a densely packed monolayer. We therefore assume that the multisulfides employed here will also fully cover a gold surface and will leave no bare gold areas.

Contact Angle Goniometry. The self-assembled monolayers of all three sulfide dendrimers G1-sulfide₄, G3-sulfide₁₆, and G5-sulfide₆₄ show relatively low advancing contact angles (Table 1), which indicate a relatively polar surface exposed to the water droplet,¹⁶ probably due to partial exposure of the polar poly(propylene imine) core. The high hystereses (θ_{ADV} minus θ_{REC}) of about 60° indicates that the alkyl chains of the molecules are not forming a well-ordered, densely packed layer. For comparison, data on a reference layer of didecylsulfide⁹ showing a hysteresis of only 21°, are included. As expected, advancing contact angles of adsorbate G4-palm₂₆-sulfide₆ are slightly higher due to the more hydrophobic nature of the alkyl chains. This shows that, in the case G4-palm₂₆-sulfide₆, and most likely also in the three cases mentioned earlier, (part of) the alkyl chains are exposed. This provides the first indication for the formation of a monolayer of surface-spread molecules on the gold interface, in which both the dialkyl sulfide chains and the amine cores are (partly) exposed.

Contact angles of SAMs of ferrocene-modified dendritic wedges Fc-G0-sulfide₁, Fc-G1-sulfide₂, Fc-G2-sulfide₄, and Fc-G3-sulfide₈ (Table 1) are similar to those obtained for the self-assembled monolayers of the whole dendrimers. This suggests that the headgroup is not important for the value of the contact angle, and supports the notion that the structures are lying flat on the surface, thus exposing the chains and amine cores to the outside bulk solution.

Monolayers of G1-sulfide₄ and G5-sulfide₆₄ on the air–water interface were prepared by the Langmuir–Blodgett technique and subsequently transferred by applying one down-and-up dipping cycle. In the ideal case, two mono-

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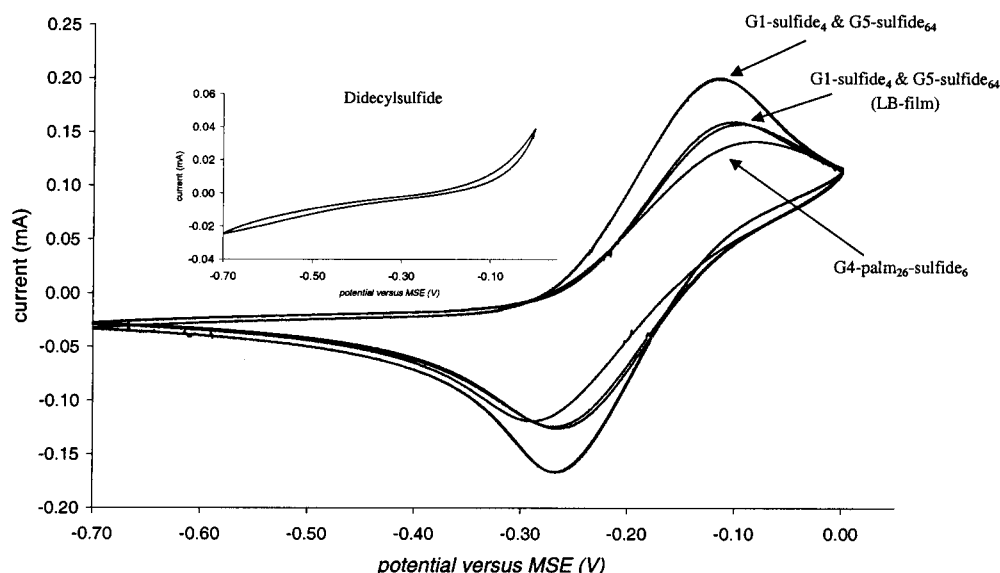


Figure 3. Cyclic voltammetric current response vs applied potential for dendritic adsorbates and $\text{CH}_3(\text{CH}_2)_9\text{S}(\text{CH}_2)_9\text{CH}_3$ on gold. The solution contains 1 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ as external redox couple in 0.1 M K_2SO_4 . The scan rate is 100 mV/s.

layers are transferred, leaving a structure in which ordered dialkyl sulfide chains (i) point toward the gold surface and the outside bulk and (ii) squeeze in an amine core layer. Experimentally, the relatively high advancing contact angles (106° and 110°) imply that the adsorbate surfaces are more hydrophobic than those of the self-assembled monolayers of the same compounds. Also, the ordering of the alkyl chains is significantly better as shown by the reduced hysteresis of $30\text{--}40^\circ$. Apparently, the transferred LB films have largely retained their original structure with closely packed alkyl chains, and thus these films provide a different architecture than that observed for the SAMs.

Electrochemical Measurements. Capacitances were determined by cyclic voltammetry for monolayers of G1-sulfide₄, G5-sulfide₆₄, and G4-palm₂₆sulfide₆, and were compared to the capacitance of a didecylsulfide monolayer. Significantly higher monolayer capacitance (C_{ML}) values ($9.3\text{--}11.0 \mu\text{F}/\text{cm}^2$) were measured for the dendrimer monolayers prepared by self-assembly from solution than for a didecylsulfide monolayer, which has a capacitance of only $5.5 \mu\text{F}/\text{cm}^2$. Monolayer capacitances provide a measure of the effective film thickness assuming that the dielectric constant remains the same. The value for the didecylsulfide SAM corresponds to a relatively well-ordered, densely packed monolayer.⁹ The higher dendrimer SAM values are in accordance with a thinner monolayer and/or a changed dielectric constant and thus to a more open (more aqueous) layer. Thus these data appear to confirm the flattened and more open structure for these adsorbates. The C_{ML} values of the transferred LB-films of G1-sulfide₄ ($7.4 \mu\text{F}/\text{cm}^2$) and G5-sulfide₆₄ ($6.6 \mu\text{F}/\text{cm}^2$), however, are almost identical to the didecylsulfide value, thus confirming their dense structure, most likely with alkyl chains standing up. The capacitance values of the adsorbates of the ferrocene-modified dendritic wedges are also comparable to those of the didecylsulfide layer, reflecting the relatively large size of the ferrocene headgroups exposed to the outside bulk.

Figure 3 shows the heterogeneous electron transfer (HET) of different adsorbate layers by means of cyclic voltammetric current response. The HET is highly sensitive to film defects, i.e., positions in the film at which the alkyl portions of the adsorbates are not well-ordered.

Electron transfer of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, selected as the electrochemical probe, through an insulating monolayer occurs via a nonadiabatic pathway.¹⁷ As the amount of defects in the film increases, the rate of electron transfer, i.e., the current, will strongly increase. As is evident from Figure 3, well-ordered monolayers of didecylsulfide (inset) block the electron-transfer almost completely. The sum of the anodic and cathodic current at the formal redox potential (-200 mV vs MSE), given as a quantitative measure, is $2 \mu\text{A}$. In contrast, SAMs of dendritic adsorbates as well as transferred LB films have lower blocking abilities against the electro-active species. The high currents found for adsorbates G1-sulfide₄ ($182.8 \mu\text{A}$) and G5-sulfide₆₄ ($173.0 \mu\text{A}$) are attributed to the open structure of the flat-lying conformation of these adsorbates. Compared to SAMs of G1-sulfide₄ and G5-sulfide₆₄, LB films of these adsorbates show less defects (144.6 and $130.2 \mu\text{A}$, respectively). The slightly lower current, determined for G4-palm₂₆sulfide₆ ($103 \mu\text{A}$), indicates a somewhat better arrangement that is possibly induced by van der Waals interactions between the alkyl chains. But even G4-palm₂₆-sulfide₆ forms monolayers with a considerable number of defects.

In compounds Fc-G0-sulfide₁, Fc-G1-sulfide₂, Fc-G2-sulfide₄, and Fc-G3-sulfide₈, the presence of the ferrocene headgroups provides us with an additional tool for characterization. The reduction and oxidation peaks in the cyclic voltammogram in the absence of an external redox couple in solution both appear at about $+0.08 \text{ V}$, and the peaks are little broadened compared to SAMs of a ferrocenethiol described before.¹⁸ Integration of the reduction and oxidation peaks can be translated directly into a surface coverage. Experimental surface coverages ranged from 9 to $63 \text{ pmol}/\text{cm}^2$ for Fc-G3-sulfide₈ to Fc-G0-sulfide₁, respectively (Table 2). These data compare well to surface coverages estimated for a model in which the molecules lie flat on the surface, and are not in line with a "standing-up" model in which the alkyl chains are packed perpendicular to the surface, and that would correspond to much higher surface coverages.

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(b) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

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Table 2. Experimental and Theoretical Surface Coverages (in pmol/cm²), Obtained from Integration of the Ferrocene Redox Signal as Measured by Cyclic Voltammetry and by Estimation from Molecular Models (20 Å² per Sulfide Alkyl Chain for the "Standing-up" Model: Cross Section of the Whole Molecule for the "Lying-Flat" Model), Respectively

adsorbate	experimental surface coverage	theoretical coverage ("standing up")	theoretical coverage ("lying flat")
Fc-G0-sulfide ₁	63	415	111
Fc-G1-sulfide ₂	45	208	55
Fc-G2-sulfide ₄	32	104	30
Fc-G3-sulfide ₈	9	52	15

Besides cyclic voltammetry, electrochemical impedance spectroscopy (EIS) was performed to characterize the dendritic adsorbate layers. The main advantage of EIS is that the layers are perturbed only with a small ac-current of 5 mV instead of the large potential sweeps used in cyclic voltammetry (−700 to 0 mV). Therefore, fragile layers are less damaged. Furthermore, the measurements can be interpreted using a model equivalent circuit to describe resistance, capacitance, etc.¹⁹ Charge-transfer resistances (R_{CT}) obtained from EIS are sensitive to the order and the number of defects of the layers. The R_{CT} values of SAMs of G1-sulfide₄ and G5-sulfide₆₄ (about 50 Ω) were 60 times smaller than those for self-assembled monolayers of didecylsulfide (3 kΩ). Actually, these values are comparable to the R_{CT} value of a bare gold electrode, thus proving the total lack of current blocking provided by these adsorbates. Even though the resistances of G4-palm₂₆-sulfide₆ (200 Ω) and of LB-films (200–300 Ω) are higher, they confirm the presence of a considerable number of defects. The values for the LB films confirm, however, the different nature of these transferred layers when compared to their SAM counterparts.

Attempts to transfer patterns using microcontact printing of G1-sulfide₄ under conditions (5 min stamp contact, feature sizes ranging from 2 to 200 μm, 60 °C, 2 min etching using ferro/ferricyanide, thiosulfate, and KOH) described before⁹ resulted in the presence of recognizable pattern edges but without the solid gold core. Apparently, high local ink concentrations at the edges results in temporary, but poor, etch resistance. This low etch resistance was to be expected from the above shown electrochemical data, especially because of the defects present in the resulting SAMs. This was further confirmed by the low etch resistance of G3-sulfide₁₆, both self-assembled from solution and after LB transfer.

All electrochemical data, as well as the contact angle measurements described above, point to the flat-lying, surface-spread nature of the dendrimer monolayers prepared by self-assembly from solution. The transferred LB-films on gold have characteristics that point to a similar structure as the one derived from the LB isotherms (Figure 2), although defects must be present (even though the transferred LB film is not a monolayer, but a double layer). Molecules with several (4–8) sulfide chains have been used in the past by us⁸ to provide well-ordered, densely packed monolayers. Therefore, we propose here that the observed flat-lying conformation of the self-assembled dendrimer adsorbates results from an additional Au–N interaction competing with the Au–S interaction. This would cause the poly(propylene imine) cores to be attracted by the gold surface as well, leading to an open and thin

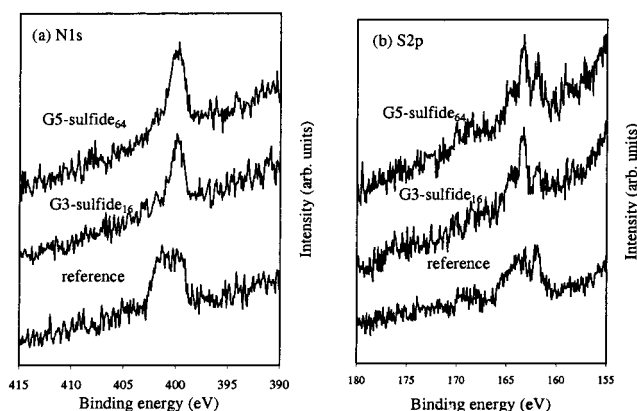


Figure 4. N_{1s} (a) and S_{2p} (b) XPS-spectra for adsorbate layers of bis(ω -aminododecyl)-disulfide (reference), G3-sulfide₁₆, and G5-sulfide₆₄ on gold; takeoff angle: 90°.

monolayer structure. Other work^{4b,20} has also shown that dendrimers without thiol or sulfide moieties, but consisting of multiple (tertiary) amines, are able to stably adhere to gold surfaces, showing that Au–N interactions are feasible, especially when cooperative binding of multiple attachment points is in play.

X-ray Photoelectron Spectroscopy. To investigate possible interaction between nitrogen atoms of the adsorbates and the gold surface, X-ray photoelectron spectroscopy (XPS) studies were performed. Figure 4, which presents the N_{1s} and S_{2p} data for G3-sulfide₁₆, G5-sulfide₆₄, and a reference layer of bis(ω -aminododecyl)disulfide, provides evidence that monolayers on gold are formed for all three adsorbates. The N_{1s} spectrum for the reference layer (Figure 4a) shows two strong components at 399.6 and 401.4 eV. For layers of G3-sulfide₁₆ and G5-sulfide₆₄ asymmetric peaks are found, suggesting the presence of the higher binding energy component for these compounds also. A possible explanation for the presence of two different nitrogen species in the reference spectra is the presence of both uncharged and charged amino groups in the film.²¹ Alternatively, a time dependent shift of the nitrogen peak (of cystamine and cysteamine) toward higher binding energy levels has been attributed to reorganization processes in the film.²² A third possibility may be a shift of the energy due to coordination of the amine to gold; a similar phenomenon is observed for sulfur.²³ This would mean that the low energy component stems from bound nitrogen, whereas the higher energy component corresponds to unbound nitrogen, demonstrating a strong interaction between the core amines and the gold substrate.

In the S_{2p} spectra of all three adsorbate films (Figure 4b), two different components can be identified. The peak at the low binding energy level (161.9 eV) is attributed to gold-bound sulfur whereas the second component, located at 163.3–163.9 eV, is attributed to unbound sulfur.²³ It is important to notice that the ratio bound/unbound sulfur for the reference layer is about 1:1. This is in general agreement with the N_{1s} spectra of the same layer showing about the same ratio of the two nitrogen peaks. This finding suggests that molecules are either oriented with the sulfur

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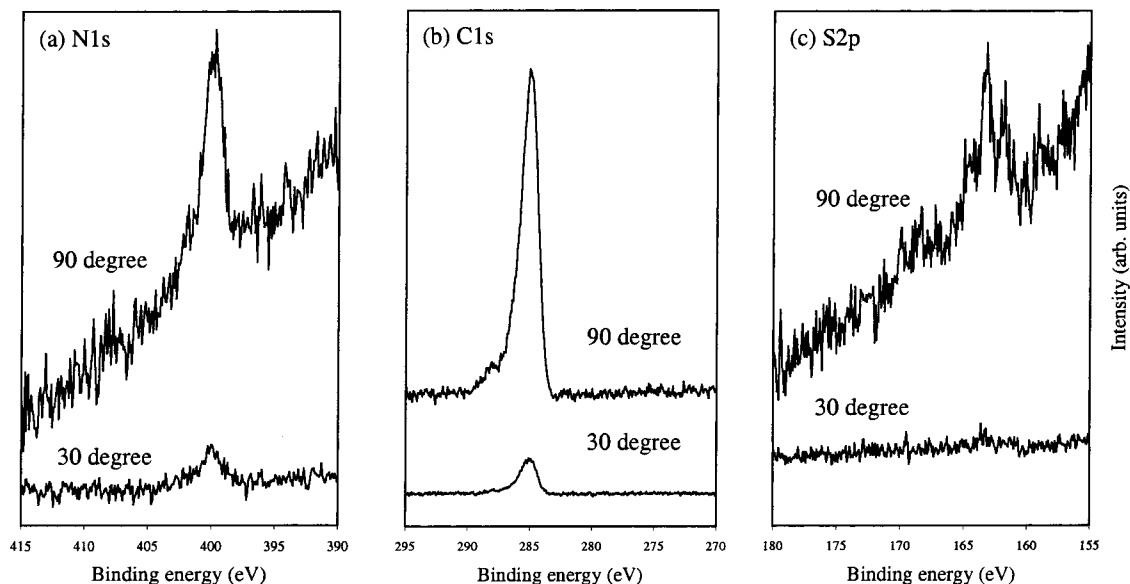


Figure 5. N_{1s} (a), C_{1s} (b), and S_{2p} (c) XPS spectra obtained with takeoff angles of 90° (top) and 30° (bottom) for adsorbate layer of G5-sulfide₆₄ on gold.

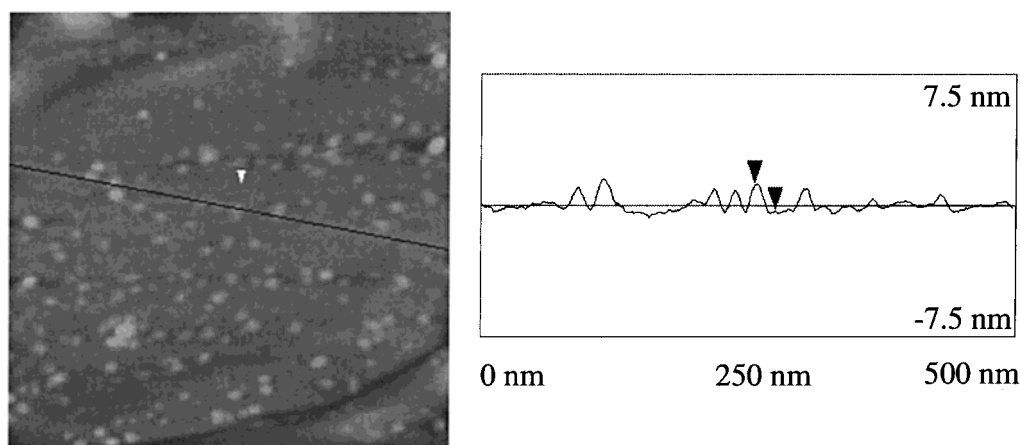


Figure 6. TM-AFM image and height profile of G1-sulfide₄ adsorbate on Au(111).

atoms or the amines to the gold surface. In case of the dendritic adsorbates, the amount of bound sulfur is lower than unbound sulfur. Ratios of about 1:2.3 and 1:1.2 were found for G3-sulfide₁₆ and G5-sulfide₆₄, respectively. This is in accordance with a higher involvement of core amines in binding, both in agreement with the N_{1s} spectra and the generally observed stronger Au–S interaction of thiolates (from adsorption of thiols and disulfides) compared to sulfides.

In an attempt to get more information on the relative distances of nitrogen, sulfur, and carbon to the gold surface in a G5-sulfide₆₄ monolayer, XPS experiments were performed with two different takeoff angles (TOA). For all three elements, a decrease of intensity was observed when using a TOA of 30° instead of 90° (see Figure 5). The relative signal decrease was about equal for all three elements showing that all three are on average equally close to the surface. This confirms the flat-lying nature of these SAMs as well as the likely involvement of the nitrogen atoms in binding to the gold substrate.

Our results imply that the flattened architecture of the SAMs of dendritic molecules can be attributed to competitive attractive forces of nitrogen and sulfur atoms to the gold surface, resulting in coadsorption of the amine core and the dialkyl sulfide chains. Accordingly, a larger

surface area per molecule than in the “standing-up” orientation is measured. Apparently, the van der Waals interactions between the alkyl chains are overcome, preventing a regular, densely packed orientation of the alkyl chains perpendicular to the gold surface.

Atomic Force Microscopy Studies. To prove the consideration that competitive attraction forces of nitrogen and sulfur atoms to gold would lead to a flat orientation of the molecules on the surface, AFM studies were performed. A prepared sample with intentional submonolayer coverage of G1-sulfide₄ shows individual dendrimer molecules (Figure 6) using tapping mode AFM. The height of only 0.5–1.5 nm of the features confirms the flattened structure of the dendrimers (an extended chain of 10 methylenes is already 1.5 nm long).

Conclusions

Dendrimers with tertiary amine and sulfide functionalities have been shown to adsorb to gold with both the sulfide chains and the amine core, leading to a flat orientation of the dendrimers on the surface. An electrochemical marker present in ferrocene-modified dendritic wedges confirms surface coverages that correspond with such a flattened orientation. In contrast, Langmuir–Blodgett layers on the air–water interface have a densely

packed structure in which the alkyl sulfide chains are aligned and the core is exposed to the aqueous phase. These layers can be transferred to gold, while largely maintaining their original structure, to yield a more dense, "standing-up" architecture on gold. Thus, we have shown that two different architectures of the same molecule can be made on a gold surface, depending on the preparation method. This can be a valuable tool in surface modification or surface patterning in particular and in nanotechnology in general.

Experimental Section

Chemicals. The synthesis and purification of didecylsulfide²⁴ and bis(*ω*-aminododecyl)disulfide²⁵ has been described elsewhere. Typical examples of syntheses are described here; the reader is referred to the Supporting Information for details on all further prepared compounds.

Modification of Poly(propylene imine) Dendrimers with Dialkyl Sulfide Chains: Illustrative Procedure for the Second-Generation Dendrimer (G2-Sulfide₈). The second-generation amine-terminated poly(propylene imine) dendrimer (328 mg, 0.42 mmol) was dissolved in dry CHCl₃ (3 mL) and added to a solution of CHCl₃ (4 mL) and the pentafluorophenylester of decylthioundecanoic acid (2.01 g, 3.83 mmol). The solution became turbid within a few minutes and was stirred at room-temperature overnight. The excess of activated ester was removed by precipitation: the reaction mixture was added dropwise to stirred hexane. The resulting suspension was centrifuged and the clear solution above the precipitate was removed by decantation. The solid was washed by three cycles of hexane addition, stirring, centrifugation and decantation. The product still contained pentafluorophenol contaminant (as evidenced by ¹⁹F NMR), which was removed by washing a chloroform solution of the product with basic water (pH = 12). The CHCl₃ layer was additionally washed with demineralized water (pH = 7), dried with Na₂SO₄ (this drying step is optional: it leads to some loss of product) and concentrated in vacuo. The product was dissolved in a small amount of CHCl₃ and precipitated in stirred MeOH. The suspension was centrifuged and the clear solution above the precipitate was removed by decantation. The solid was washed by one additional cycle of MeOH addition, stirring, centrifugation and decantation. Finally, the collected product was dried in a vacuum oven and stored in a glovebox under a N₂ atmosphere. Yield: 1.0 g (67%) of a white solid. ¹H NMR (CDCl₃/CD₃OD = 10/1, ppm): δ = 7.2 and 3.7 (8H, NHCO), 3.2 (16H, t, CH₂NHCO), 2.5 (32H, t, CH₂SCH₂), 2.4 (36H, m, N(CH₂), 2.2 (16H, t, CH₂CONH), 1.7–1.5 (72H, m, NCH₂CH₂CH₂N, CH₂CH₂SCH₂CH₂, CH₂CH₂CO), 1.4–1.2 (212H, m, remaining methylene hydrogens), 0.95 (24H, t, CH₃). ¹³C NMR (CDCl₃/CD₃OD = 10/1, ppm): δ = 174.2 (8C, NHCO), 53.9 (2C, NCH₂CH₂CH₂CH₂N), 51.9 (4C), 51.8 (4C), 51.1 (8C, NCH₂CH₂CH₂NHCO), 37.5 (8C, CH₂NHCO), 36.3 (8C, CH₂CO), 31.9 (16C, CH₂SCH₂), 31.7 (8C, CH₂CH₂CH₃), 29.5 (16C), 29.3 (32C), 29.2 (16C), 29.1 (16C), 29.0 (8C), 28.7 (16C), 26.4 (8C, CONHCH₂CH₂CH₂N), 25.7 (8C, COCH₂CH₂), 24.4 (2C, NCH₂CH₂CH₂CH₂N), 23.7 (4C, (–CH₂CH₂)₂NCH₂CH₂CH₂CH₂N(CH₂CH₂)₂), 22.4 (8C, CH₂CH₃), 13.8 (8C, CH₃). C₂₀₈H₄₁₆S₈O₈N₁₄ (FW = 3497.8). Elemental analysis. Found: C = 71.72, H = 12.22, N = 5.65. Calcd: C = 71.42, H = 11.99, N = 5.61. MALDI-TOF-MS: isotope clusters are observed at [M+H]⁺ = 3498, [M+Na]⁺ = 3520, and [M+K]⁺ = 3536.

Preparation of Ferrocene-Substituted Amine-Terminated Poly(propylene imine) Dendrimers: Typical Repetitive Procedure Shown for Fc-G1-NH₂. To a solution of Fc-G0-NH₂ (876 mg, 3.06 mmol) in water (30 mL) was added acrylonitrile (5.07 mL, 76.4 mmol) at room temperature. The solution was refluxed overnight. Subsequently, the solution was acidified by 0.1 N HCl and extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and concentrated, yielding

a brown solid (Fc-G1-CN; yield: 1.08 g, 2.76 mmol, 90%). ¹H NMR (CDCl₃): δ = 6.24 (s, 1H, NHCO), 4.75–4.65 (m, 2H, Cp-H₃₊₄), 4.40–4.30 (m, 2H, Cp-H₂₊₅), 4.22 (s, 5H, C₅H₅), 3.60–3.40 (m, 2H, CH₂NHCO), 2.93 (t, 4H, J = 6.6 Hz, CH₂CN), 2.70 (t, 2H, J = 6.5 Hz, CH₂N), 2.56 (t, 4H, J = 6.6 Hz, CH₂N), 1.90–1.75 (m, 2H, CH₂). MS (FAB-MS) *m/z*: 392.1 ([M]⁺). Calcd for C₂₀H₂₄N₄OFe: 392.1. To 30 mL of a 1.4 M solution of NaOH in EtOH/H₂O (95:5) and Fc-G1-CN (168 mg, 428 μmol) was added Raney-nickel (1.0 g). The mixture was refluxed under H₂ (normal pressure) for 3 h. The catalyst was filtered and washed with ethanol. After addition of H₂O, the ethanol was evaporated. The residue was extracted several times with dichloromethane. The organic layers were dried with Na₂SO₄ and the solvent was evaporated in vacuo to give Fc-G1-NH₂ (153 mg, 382 μmol, 89%). ¹H NMR (CDCl₃): δ = 6.20 (s, 1H, NHCO), 4.75–4.65 (m, 2H, Cp-H₃₊₄), 4.40–4.30 (m, 2H, Cp-H₂₊₅), 4.21 (s, 5H, C₅H₅), 3.75–3.35 (m, 2H, CH₂NHCO), 2.85–2.70 (m, 4H, CH₂ NH₂), 2.60–2.45 (m, 6H, CH₂N), 1.80–1.60 (m, 6H, CH₂). MS (FAB-MS) *m/z*: 401.2 ([M+H]⁺). Calcd for C₂₀H₃₂N₄OFe: 400.2).

Modification of Ferrocene-Substituted Amine-Terminated Poly(propylene imine) Dendrimers with Dialkyl Sulfide Chains: Illustrative Procedure for the Zeroth-Generation Dendrimer (Fc-G0-sulfide₁). To a solution of 11-(4-nitrophenyloxyformamido)undecyldecylsulfide (47 mg, 93 μmol) and Fc-G0-NH₂ (32 mg, 112 μmol) in dichloromethane (13 mL) was added diisopropylethylamine (19.5 μL, 112 μmol) and a catalytic amount of *N,N*-(dimethylamino)pyridine. The solution was stirred at room-temperature overnight. Subsequently, the solution was washed with 0.1 N HCl and 10% NaOH and brine. The organic layer was dried over Na₂SO₄ and condensed. The crude compound was purified by TLC (silica; eluent: 5% MeOH in dichloromethane), giving Fc-G0-sulfide₁ as a yellow solid (yield: 47 mg, 72 μmol, 64%). mp: 80 °C. ¹H NMR (CDCl₃): δ = 7.03 (t, 1H, NH–CO–Fc), 5.16 (t, 1H, NHCONH), 4.85–4.75 (m, 2H, Cp-H₃₊₄), 4.58 (t, 1H, 5.4 Hz, NHCONH), 4.40–4.30 (m, 2H, Cp-H₂₊₅), 4.23 (s, 5H, C₅H₅), 3.50–3.10 (m, 6H, CH₂NH), 2.52 (t, 4H, J = 7.3 Hz, CH₂S), 1.75–1.45 (m, CH₂CH₂NH, CH₂CH₂S), 1.45–1.20 (m, 28H, CH₂), 0.90 (t, 3H, J = 6.6 Hz, CH₃). MS (FAB-MS) *m/z*: 655.5 ([M]⁺). Calcd for C₃₆H₆₁N₃O₂SFe: 655.4).

Self-Assembled Monolayer Preparation. Gold substrates were produced by evaporation of a 2 nm chromium layer and 200 nm of gold on a polished glass slide (Ø 25 mm). Before use, the gold substrates were cleaned in oxygen plasma for 5 min and left for 15 min in ethanol. All glassware used for monolayer preparation was cleaned with piranha.²⁶ The cleaned gold substrates were immediately immersed in a 0.1 mM solution of dendritic adsorbates in ethanol: chloroform (1:2) for 12 h. SAMs of dendrimers were prepared at 60 °C. Afterward, the substrates were rinsed with large amounts of chloroform, ethanol, and water.

Langmuir–Blodgett Film Preparation. Monolayer experiments were performed on a thermostated, home-built trough at 20 °C. The surface pressure was measured using the Wilhelmy plate method using filter paper. On the water subphase a CHCl₃ solution of the dendrimer of typically 25–50 μL was spread and the solvent was allowed to evaporate. The isotherms of Figure 2 were recorded with a 140 cm² trough, applying a compression rate of about 5 mm²/s. LB film transfer to a gold surface was executed with a larger 1100 cm² trough by consecutive (vertical) down-and-up dipping of a round-shaped gold substrate that was previously treated with piranha,²⁶ washed with 18 MΩ water and EtOH, and dried. For G1-sulfide₈ and G5-sulfide₆₄, the transfer was executed after compression at constant surface pressures of 21.5 and 19.0 mN/m, respectively; the dipping lasted for a total of about 15 min in both cases. During down-dipping a high contact angle of the water with the gold surface was observed (dewetting), whereas up-dipping gave a low contact angle (wetting). On the basis of these observations, it is expected that two monolayers are transferred onto the gold, creating an architecture with the dialkyl sulfide chains facing both the gold and the air and with a sandwiched amine core layer (in fact, a double amine core layer).

Instrumentation. Wettability of the SAMs by water was determined with a Krüss (Hamburg, Germany) G10 goniometer

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(26) Warning: Piranha solution—a 3:1 mixture of H₂SO₄ and H₂O₂ solution—should be handled with caution; it has detonated unexpectedly.

equipped with a motorized pipet. Each value was deduced from five sets of advancing and receding angles, each at a different spot of the same sample, measured on three different samples. Cyclic voltammetry and impedance spectroscopy was performed on an Autolab GSTAT10 (ECOCHEMIE, Utrecht, The Netherlands). The measurement device consists of a three-electrode cell consisting of a gold working electrode (area = 0.44 cm²), a platinum counter electrode and a mercuric sulfate reference electrode (+0.61 V_{NHE}). Capacitances were determined by cyclic voltammetric measurements in 0.1 M NaClO₄ between -0.4 and -0.3 V_{MSE} at scan rates of 0.1, 0.2, and 0.5 V/s. Heterogeneous electron-transfer measurements and impedance spectroscopy were conducted using an external redox couple (1 mM K₃Fe(CN)₆/K₄Fe(CN)₆) in 0.1 M K₂SO₄. As the value for the heterogeneous electron transfer, the sum of the anodic and cathodic current (HET) at the formal potential of the redox couple (-0.2 V_{MSE}) of the cyclic voltammetric measurements (-0.7 V to 0.0 V; scan rate: 0.1 V/s) is reported. The charge-transfer resistances are determined by impedance spectroscopy. Therefore, we scanned at -0.2 V_{MSE} with an amplitude of 5 mV using a frequency range from 50 kHz to 0.1 Hz. Spectra were evaluated by fitting the experimental data to an equivalent circuit containing ohmic resistances in parallel and in series and a capacitive resistance.²⁷ For X-ray photoelectron spectroscopy (XPS) a VG Escalab 220I-XL instrument was used with a monochromatic Al K α X-ray source. XPS data were collected from a surface area of 150 $\times$ 150 nm² with a pass energy window of 20 eV. AFM images were acquired on a NanoScope II multimode AFM (Digital Instruments (DI), Santa Barbara, CA) operated in tapping mode. A PerSeptive Biosystems Voyager DE PRO MALDI-TOF mass spectrometer,

a Varian Gemini 300 MHz or a Varian Mercury Vx 400 MHz NMR spectrometer, a PE 2400 elemental analyzer, a PE Spectrum One ATR-FTIR spectrometer was used and FAB-MS was performed on a Finnigan MAT 90 spectrometer.

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Supporting Information Available: In addition to the synthetic and analytical information given in the Experimental Section of this article, further synthetic procedures and analytical details on all prepared compounds supplied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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