

Formation of nanorods by self-assembly of alkyl-substituted polyphenylene dendrimers on graphite

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Alkyl-substituted polyphenylene dendrimers with a tetrahedral or disk-like shape form self-assembled monolayers on graphite (HOPG) which show complex supramolecular structures, such as parallel rods of 6 nm diameter or two-dimensional crystals.

The construction of supramolecular structures by self-assembly of molecules is a topic of great current interest in relation to the fabrication of new materials.^{1–3} Dendrimers are attractive building blocks to form such materials because they are monodisperse macromolecules with well-defined shapes and dimensions.^{4,5} In this paper, we report on the structure of self-assembled dendritic monolayers on the basal plane of graphite. Dendrimers binding to graphite are the ideal model system to study the adsorption of macromolecules to surfaces because adsorbant and adsorbent are well defined.

Different dodecyl-substituted polyphenylene dendrimers were synthesized (Fig. 1) and monolayers were formed by spontaneous adsorption from solution on the basal plane of graphite. The structure of these monolayers was imaged with an atomic force microscope (AFM). Formation of self-assembled dendritic monolayers is possible because the alkyl chains adsorb strongly to graphite; the adsorption energy is roughly 7 kJ

mol⁻¹ per methylene unit.^{6,7} In addition, each phenylene subunit in close contact with the graphite surface is expected to contribute an adsorption energy of roughly 15 kJ mol⁻¹.⁸

Dendrimers **1** and **2** were prepared divergently *via* reiterative Diels–Alder cycloaddition according to the procedure described in ref. 9. The synthesis starts from a polyfunctional central building block, tetra(4-ethynylphenyl)methane for **1**, and 1,3,5-triethylbenzene for **2**. To introduce dodecyl alkyl chains on the periphery of the dendrimer, tetraphenylcyclopentadienones alkylated with dodecyl chains were added by Diels–Alder cycloaddition as the last layer of the dendrimer. The dendrimers were characterized by MALDI-TOF mass spectrometry, NMR spectroscopy and GPC, and revealed that the products were pure. Due to the polyphenylene backbone and the high number of twisted, interlocked benzene rings, these dendrimers show a high shape persistence, with diameters of 5.5 and 3.8 nm for dendrimers **1** and **2**, respectively.¹⁰ According to force field calculations and X-ray diffraction studies, dendrimer **1** shows a tetrahedral structure, whereas dendrimer **2** has a more planar propeller-like structure (Fig. 1).^{11,12}

Dendrimer layers were prepared with the spin coating technique. A drop of solution was deposited on a freshly cleaved HOPG (highly oriented pyrolytic graphite) substrate and the

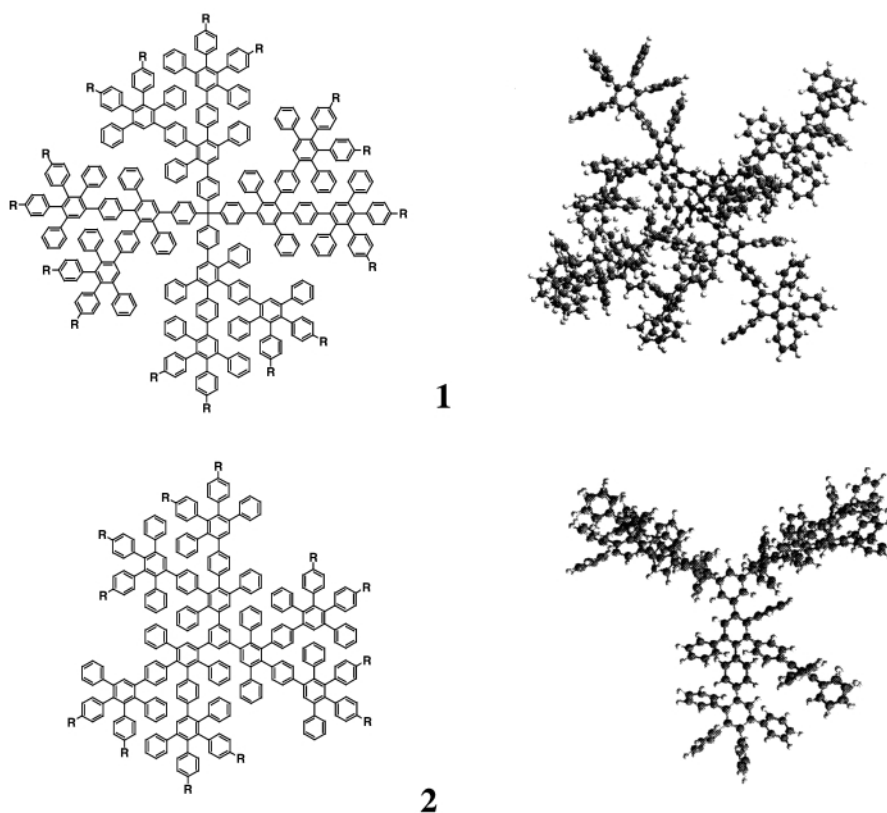


Fig. 1 2D- and 3D-structure (MM2 molecular mechanic simulation with CERIU2 program package, Molecular Simulations Inc., Waltham, MA, USA) of the investigated alkyl-substituted polyphenylene dendrimers; R=C₁₂H₂₅.

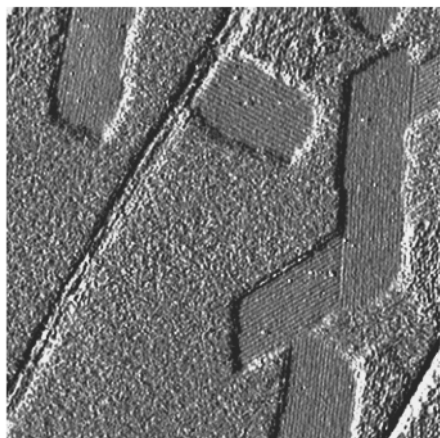


Fig. 2 AFM amplitude image (scan size 639 nm) of a dendrimer **1** layer on HOPG.

sample was rotated at 810 rpm for 10 s. Dendrimers were dissolved in dichloromethane at a concentration of 0.002 mg ml^{-1} ($2.7\text{--}4 \times 10^{-7} \text{ M}$). Samples were imaged at room temperature with a commercial AFM (Nanoscope III, Digital Instruments, Santa Barbara, California) in tapping mode using rectangular silicon cantilevers (Nanosensors, $125 \mu\text{m}$ long, $30 \mu\text{m}$ wide, $4 \mu\text{m}$ thick) with an integrated tip, a nominal spring constant of 42 N m^{-1} , and a resonance frequency of 330 kHz.

When preparing layers of dendrimer **1**, most of the graphite surface was covered with a diffuse layer. In addition, some distinct structures were observed. Some of the most remarkable structures were regions covered by parallel rows of $5.9 \pm 0.7 \text{ nm}$ spacing (Fig. 2). Typically, the regions were $50\text{--}100 \text{ nm}$ wide and $70\text{--}800 \text{ nm}$ long. Usually only a few percent of the total surface area was covered with a rod-like structure. However, in 2 out of 11 experiments, almost the whole surface was covered by rods. The rods were stable and could be imaged for several hours. Different rod-like regions were oriented parallel (0°) or at 60° or 120° with respect to each other. This indicates that the underlying graphite with its hexagonal structure determines the orientation of the dendrimer rods.

When forming monolayers from dendrimer **2**, in 4 out of 6 experiments, two-dimensional crystals (Fig. 3) were formed. The primitive unit cell can be described by the lattice constants $a = 10.2 \pm 0.3$, $b = 7.4 \pm 0.4 \text{ nm}$ and an angle of $122.8 \pm 2^\circ$. Like the rod-like regions, these lattices were oriented parallel (0°) or at 60° or 120° with respect to each other, indicating that the underlying graphite determines their orientation. Each unit cell probably contains at least two molecules. This is indicated by the unit cell area of 63 nm^2 . An upper limit for the area

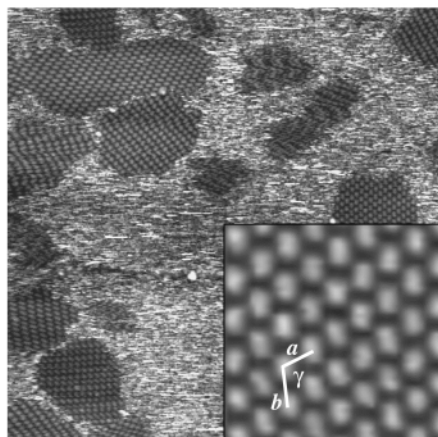


Fig. 3 AFM height image of a dendrimer **2** layer on HOPG showing a region with two-dimensional crystals (scan size 578 nm, 1 nm height). The insert shows details of a crystal. The lattice constants are indicated.

occupied by one dendrimer can be estimated from the extension of a polyphenylene chain with 10 phenylene rings plus two dodecyl chains, which is roughly 6 nm. When hexagonally close packed, circles of 6 nm diameter would occupy an area of 31 nm^2 . In addition, each protrusion in a unit cell had an elongated, oval and not spherical shape. This shows that individual molecules do not form separate units, but that real supramolecular structures are formed. The two-dimensional crystals were stable and could be scanned many times. In one experiment we observed rod formation, as with dendrimer **1**. The spacing between the rods was again 6 nm. The rods were not stable and disappeared after scanning them few times.

The formation of rods on surfaces has been observed from dendritic nanorods.¹³ However, to the best of our knowledge, this is the first observation of rod formation from the self-assembly of dendrimers which are tetrahedral (dendrimer **1**) or shaped like a disc (dendrimer **2**) in solution.

Since it is a requirement for the formation of regular structures, it is ideally that single dendrimers on bare graphite are mobile. Hydrocarbon chains are strongly adsorbed to graphite and, once they are adsorbed, it is unlikely that they can leave the surface spontaneously. They can, however, diffuse laterally. Computer simulations of individual alkyl chains on graphite revealed negligible activation energy for translation along the chain.⁶ The same is true for the polyphenylene subunits, because benzene molecules are able to diffuse laterally, even at temperatures of 85 K.¹⁴ Hence, the dendrimers can probably diffuse on bare graphite. This explains why we were never able to image half-covered graphite. Either the surface was totally clean (this was the case when preparing layers from concentrations of $<0.002 \text{ mg ml}^{-1}$) or an almost complete monolayer was observed.

The requirement of high lateral mobility also explains why thiol-substituted dendrimers on gold do not form regular structures.² They bind to gold and remain at the point of first encounter, held by the strong localised thiol-gold bond. In contrast, dendrimers which form a monolayer at the air-water interface and which are laterally mobile also show two-dimensional crystalline packing.¹⁵

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