

## Structural Distortion of Dendrimers on Gold Surfaces: A Tapping-Mode AFM Investigation

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Received December 18, 1997

We report an atomic force microscopy (AFM) investigation of generation 4 and 8 (G4, G8) polyamidoamine (PAMAM) starburst dendrimers adsorbed on Au (111) surfaces. Heights measured for isolated, adsorbed dendrimers indicate they are substantially more oblate than expected from their spherical shapes in solution. By controlling dendrimer concentration and exposure time during adsorption, modified surfaces ranging from isolated molecules to near-monolayer coverages were obtained. Exposure of surfaces bearing adsorbed isolated dendrimers to hexadecanethiol solutions changed their conformation from oblate to prolate as more stable thiol–Au bonds replaced some of the amine–Au bonds. For surfaces of near-monolayer coverage, exposure to hexadecanethiol caused the dendrimers to gradually agglomerate, forming dendrimer “pillars” up to 30-nm high.

There is a vast literature pertaining to dendrimers,<sup>1</sup> but only a few reports of individual dendrimer visualization using TEM,<sup>2</sup> STM,<sup>3</sup> and AFM,<sup>4,5</sup> or showing the grainy structure of a dendrimer monolayer using AFM.<sup>6</sup> For our study, dendrimers<sup>7</sup> were adsorbed onto atomically flat Au (111) facets by dipping the substrate<sup>8</sup> into either a 10<sup>−7</sup> M ethanolic solution (for monolayers) or a 10<sup>−9</sup> M solution (for isolated molecules) for 45 s. Au substrates were then alternately rinsed with ethanol and water. To alter the shape of isolated dendrimers, samples were soaked for 4 h in a 1 mM ethanolic solution of hexadecanethiol and then rinsed as described above. To induce agglomeration, dendrimer monolayers were soaked in hexadecanethiol solution for 24–110 h. Measurements made in a minimum of three different areas within each of five well-separated 10 × 10 μm sites on each of two identically prepared Au substrates (30 areas altogether) yielded consistent results. Tapping-mode AFM measurements (topographical data only) in air were performed using a Nanoscope III STM with an E-type scanner.<sup>9</sup>

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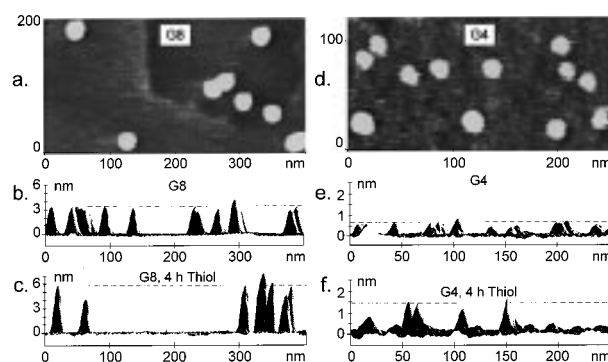
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(7) Starburst PAMAM dendrimers, along with supporting technical data, were generously provided by Dendritech, Inc., Midland, MI.

(8) Au substrates were prepared by melting and flame annealing wires to form Au balls having single-crystalline (111) facets. See: Zamborini, F. P.; Crooks, R. M. *Langmuir* **1997**, *13*, 122–126 and references therein.



**Figure 1.** Top-view topographical images of (a) G8 and (d) G4 dendrimers distributed on a Au (111) surface. Profiles of images shown in a and d are provided in parts b and e. After exposure to hexadecanethiol for 4 h, the profiles shown in c and f (same surface, but different region) result for G8 and G4 dendrimers, respectively.

We investigated two different sizes of dendrimers: the soft and deformable G4 (ideal sphere diameter, 4.5 nm) and the larger G8 having a harder exterior (ideal sphere diameter, 9.7 nm).<sup>7</sup> The results for G8 are displayed in parts a–c of Figure 1. Figure 1a shows the topography of the Au surface covered with isolated G8 dendrimers. In the upper right corner, an Au step edge is visible, its height (0.24 nm) providing a vertical reference scale. The measured diameter of the adsorbed G8 dendrimer is approximately 20 nm, but as discussed below, the lateral dimensions are convoluted with the AFM tip shape. Nevertheless, the height data in Figure 1b are reliable. Within experimental error (0.1–0.2 nm) and on the basis of data from more than 100 single dendrimers, the height of the G8 dendrimers on a naked Au surface ranges from 3.5 to 4.0 nm, or about 60% less than the ideal-sphere diameter of 9.7 nm. The variation in height and lateral size of the surface-confined dendrimers may arise from a distribution of molecular sizes resulting from the synthesis,<sup>2b</sup> tip-induced deformation of the dendrimers,<sup>6,10–12</sup> and/or differences in adsorption geometry. Tsukruk et al. reported the thickness of G6 monolayers adsorbed to Si as 2.8 nm and of G10 monolayers as 5.6 nm,<sup>6</sup> which are comparable to our results for G8 on Au. A possible explanation for the discrepancy between measured and ideal-sphere diameters is the attachment of the dendrimers to the surface via a number of Au–amine bonds<sup>13</sup> (in contrast to the weak mica- or graphite-carbosiloxane dendrimer interactions,<sup>4</sup> for which deviations from ideal-sphere diameter are reportedly minor). This “multipoint attachment” is more pronounced for isolated dendrimers than for full monolayers, where intermolecular interactions between dendrimers affect conformation.

Figure 1c shows the profile of adsorbed G8 dendrimers after soaking for 4 h in hexadecanethiol. The surface density generally diminishes, some dendrimers having been replaced completely by the alkanethiols: the amine–Au interactions are challenged by stronger thiol–Au bonds. The height of the dendrimers

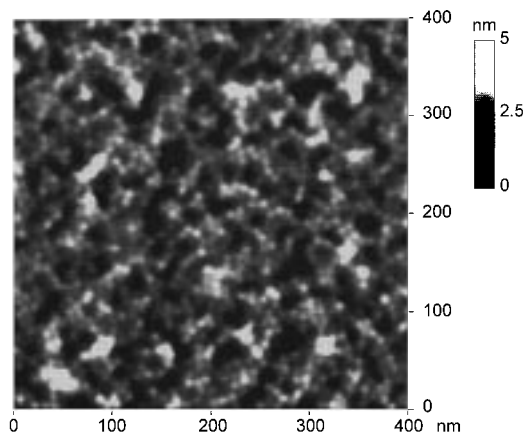
(9) Tapping-mode cantilevers (Digital Instruments, Santa Barbara, CA) had resonance frequencies of 260–280 kHz, force constants of 20–100 N/m, and tip apex radii from 5 to 10 nm. The cantilevers were operated at an  $A_0$  of 4 V (40–60 nm) and a ratio of  $A_{SP}/A_0$  of 0.8, corresponding to “slight tapping” (see ref 10). The scan rate for images of all sizes was 2 Hz. Images included 512 × 512 data points and were flattened after recording using algorithms contained in the software; a low-pass filter was applied once.

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**Figure 2.** Topographical image of a G8 monolayer on Au (111); individual G8 dendrimers are discernible. The scale bar is relative, not absolute, because the tip does not contact the Au surface.

remaining on the surface increases reproducibly from 3.5–4.0 to 5.0–6.5 nm. The noise and uncertainty of the 0-nm level also increase due to the presence of the thiol layer.<sup>14</sup> The length of the hexadecanethiol chains is approximately 2 nm, and our 5.0–6.5-nm height range was measured from the terminal methyl groups; thus, the height of the dendrimers is 7.0–8.5 nm after correcting for the thickness of the hexadecanethiol layer. This agrees well with independently measured spectroscopic data.<sup>13</sup> While it is difficult to estimate how much the thiols or dendrimers are deformed by the tapping tip, interfacial force microscopy indicates that the frequency and vertical velocity of the vibrating tip are probably too high to cause kinks in the alkane chains or severe deformations of the dendrimer shapes.<sup>15</sup> With or without correction for the alkanethiol layer, the increase in dendrimer height is significant.

Thus, thiol adsorption results in a significant increase in the height of the dendrimers as they lose amine–Au links and allows dendrimers that were initially firmly anchored to be pushed about on the thiol-modified surface by the low-contact-force tapping tip, as previously reported for low-energy surfaces.<sup>4</sup> The compressed state is relatively stable: 24 h in hexadecanethiol solution does not affect the height of the remaining isolated dendrimers. However, extended exposure to a hexadecanethiol solution leads to complete displacement of the dendrimers by the thiols.<sup>16</sup>

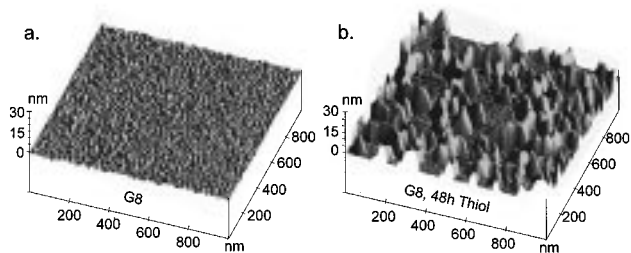
Parts d–f of Figure 1 show data for G4 dendrimers corresponding to that just discussed for G8. The measured height of the G4 dendrimers on a naked Au surface is 0.5–0.8 nm (cf. 1.8 nm for a G4 monolayer in ref 6). Again, the lateral dimension (ca. 15 nm) is convoluted with the tip shape. Exposure of the Au substrate to hexadecanethiol results in a height increase of the G4 dendrimers to 1.4–2.0 nm above the thiol level, or about 3.5–4.0 nm overall.

Figure 2 shows a freshly prepared G8 dendrimer monolayer composed of aggregates of discernible individual dendrimers (black areas correspond to the naked Au surface). In striking contrast to Figure 1, no isolated dendrimers are observed anywhere

(14) Scraping away the adsorbate with the tip to obtain a 0-nm level is not reliable. (see: Thomas, R. C.; Houston, J. E.; Michalske, T. A.; Crooks, R. M. *Science* **1993**, 259, 1883–1885).

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(16) All results reported here pertain to 45-s dendrimer adsorption times onto a near-perfect Au(III) surface. As reported elsewhere (see ref 13), longer dendrimer adsorption times lead to more stable mixed monolayers.



**Figure 3.** Height plots of (a) a G8 monolayer on naked Au, and (b) after soaking in an ethanolic hexadecanethiol (1 mM) solution for 48 h. As the thiol occupies more of the surface, the dendrimers aggregate into progressively higher pillars.

on the surface, only aggregates or strings composed of several interconnected dendrimers. Apparently intermolecular interactions between dendrimers, either hydrogen bonds between the terminal groups or physical interdigitation of the branches (not observed in solution),<sup>17</sup> help to stabilize the monolayer.

In comparing the size of the G8 dendrimers in Figures 1 and 2, the lateral dimensions of isolated dendrimers appear much larger than in the monolayer, a consequence of the convolution of the tip shape with that of the dendrimer.<sup>18</sup> Because their height is 3.5–6.5 nm above the respective 0-nm level, the isolated G8 dendrimers are contacted only by the tip's apex (radius, 5–10 nm).<sup>9</sup> To a first approximation, this corresponds to a spherical tip riding over deformed spheres (dendrimers) of comparable size, resulting in the addition of about twice the tip radius to the actual lateral dimensions of the isolated dendrimers. This consideration does not hold for the smaller G4 dendrimers, for which much less than twice the tip radius is added.<sup>4,19</sup> In the case of monolayers, the tip does not reach the Au surface, riding instead on the tops of the dendrimers, the result being negligible addition to the lateral dimensions.

In Figure 3, the results of exposing a monolayer of G8 to hexadecanethiol are presented. Figure 3a shows a G8 monolayer similar to that in Figure 2: the surface has a grainy structure with 3–4-nm corrugations.<sup>14</sup> After a 48-h exposure to hexadecanethiol, the picture changes completely: the dendrimers vacate the surface in favor of the thiols, piling up to form aggregates reaching heights of 15–18 nm; individual dendrimers are no longer recognizable.<sup>16</sup> This aggregation, as opposed to loss of the dendrimers into solution, demonstrates the relatively strong intermolecular forces between surface-bound dendrimers. After 110 h, even more of the surface is covered by the thiols and the height of the aggregates increases to 25–30 nm. Concurrently, the surface area covered by the dendrimers decreases drastically. After 110 h, it is again possible to image the Au step edges in the areas covered by the thiol. After extended exposure, the surface is fully thiol-covered and devoid of dendrimers.<sup>16</sup>

**Acknowledgment.** A.H., J.K.C., L.A.B., and R.M.C. gratefully acknowledge the National Science Foundation (CHE-9313441) and the Robert A. Welch Foundation for support of this work. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

JA974283F

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