

Formation of robust mesoscopic ring structures by self-assembly of SiCl₃-terminated dendrimers

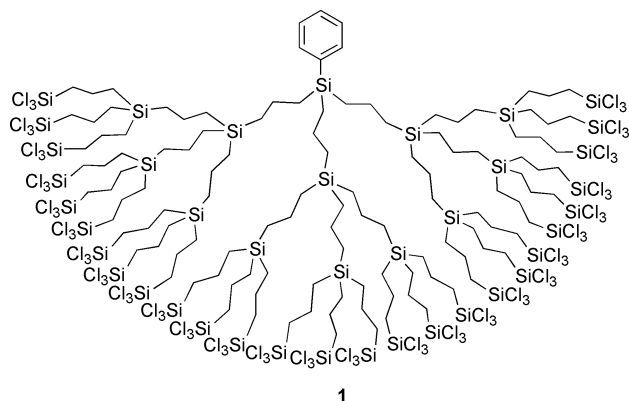
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Robust sub-micrometer ring structures are easily prepared using SiCl₃-terminated dendrimers.

The formation of submicrometer-scale structures *via* the self-assembly of molecules is of great current interest.¹ Recently, several groups have reported the formation of mesoscopic ring structures on solid surfaces using a variety of materials, including porphyrin derivatives, nanoparticles, and carbon nanotubes.^{2–6} These ring structures were easily formed after the evaporation of a dilute solution of the materials deposited on substrate surfaces, through an intermediate morphology featuring droplets or holes. Unfortunately, the molecules/particles in these structures were held together only through weak intermolecular interactions. Consequently, the structures possess a limited stability that restricts their potential applications. During the course of systematic investigation of the chemisorption of a series of SiCl₃-terminated dendrimers on flat surfaces, we observed that the films of **1** deposited on mica spontaneously



adopted well-defined sub-micrometer ring structures across the surface. Notably, the dendrimers in the films polymerize upon curing, thereby affording robust and highly stable ring structures.

The ring structures were easily and reproducibly prepared by spin coating of a 10⁻⁵ M solution of **1** in anhydrous THF on a freshly cleaved mica substrate. As revealed by AFM (Fig. 1), the isolated rings are randomly located over the entire substrate surface. Most of the rings possess an inner diameter of 450–550 nm. Although rings dominate the film surface, separated islands with a bottom diameter of 110–230 nm and a height of 2.0–3.5 nm are also present; these are located predominately outside the rings and on the rims. Root mean square roughness (R_q) measurements show that the film surface inside the rings ($R_q = 0.160$ nm) is much flatter than outside ($R_q = 0.530$ nm). Fig. 2 depicts a typical ring and a cross sectional plot of the ring diameter (R), height (h), and width (L) of the rim. Notably, the rims of all the rings possess a similar average width ($L \approx 150$ nm) and height ($h \approx 4–6$ nm). Interestingly, the layer outside the rings is higher than that inside by $D \approx 1.1$ nm (Fig. 2). To measure the thickness of the layer inside the rings, part of the film was shaved by AFM using a square pyramid Si₃N₄ probe

with a loading force of *ca.* 190 nN. Fig. 3 shows an AFM image of the region containing the shaved area. The average thickness of the flat layers outside and inside the rings was then measured

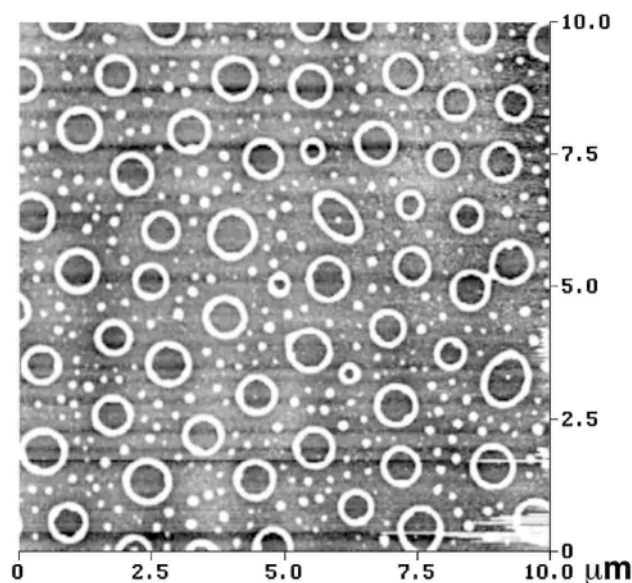


Fig. 1 An AFM image of a thin film formed by spin-coating of a THF solution of **1** onto a mica surface. The contrast covers height variations in the 0–15 nm range.

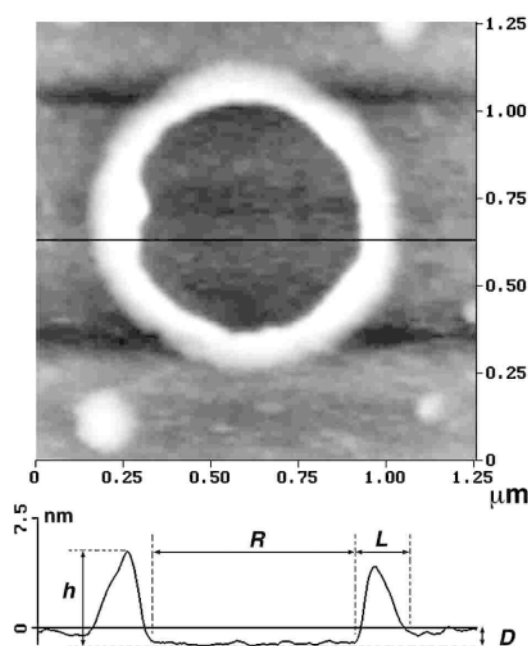


Fig. 2 An AFM image of a ring and a line scan for measurement of the ring diameter (R), height (h), and width (L) of the rim.

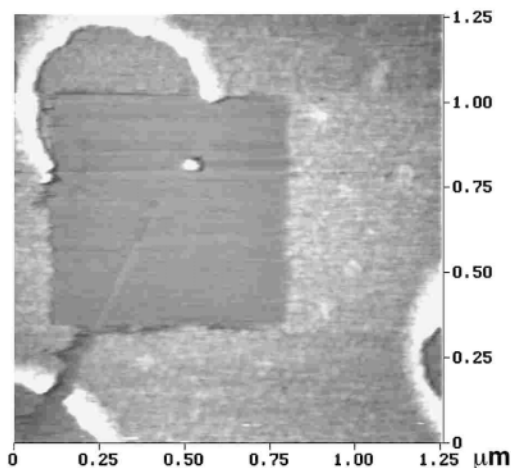


Fig. 3 Tapping mode AFM image of a film region containing an area shaved by contact mode AFM.

by AFM to be 2.2 ± 0.4 nm and 1.3 ± 0.3 nm, respectively. The former corresponds to a monolayer of densely packed dendrimers, as the height of **1** is calculated to be *ca.* 2.2 nm by molecular mechanics (MM2). The latter could correspond to a monolayer of flattened dendrimers. It is well known that flexible dendrimers can substantially flatten on a surface when their interaction with the surface is strong.⁸

Upon deposition of **1** (dissolved in THF) on mica in air, the SiCl₃ groups of **1** should be completely hydrolyzed to Si(OH)₃ groups by surface-bound and absorbed water.⁹ Intermolecular condensation of the Si(OH)₃-terminated dendrimers may occur at room temperature, but apparently only to a limited extent. In fact, films that were kept at room temperature in air for two weeks can still be shaved by AFM. Although they cannot covalently bond to the mica surface which does not contain OH groups, the dendrimers can undergo substantial condensation to form a cross-linked network of Si–O–Si groups at elevated temperatures.⁹ Indeed, after curing at 115 °C for 12 h, the unchanged ring structures became robust; they could no longer be scratched by AFM tips, even under a loading force as high as 250 nN. In addition, they remained intact after storage in air for months, and after repeated washing with water and organic solvents such as THF and chloroform.

Despite the presence of a large number of hydrophilic Si–O–Si groups in the dendrimers after hydrolysis and curing, the surface of the cured films possessed a surprisingly high water contact angle (advancing: 103°; receding: 92°; static: 100°) and hexadecane contact angle (advancing: 38°; receding: 31°; static: 35°). These contact angles are similar to those for a smooth solid surface exposing closely packed –CH₂– or –CH=CH₂ groups.¹⁰ In addition, force measurements by AFM showed that the attraction forces between the Si₃N₄ tip and the film were nearly the same inside and outside the rings, indicating a similar composition for both surfaces. These results suggest that the dendrimer molecules fully cover the hydrophilic mica surface with all of their SiOR groups (R = H, OSi), leading to a hydrophobic film surface composed mostly of –CH₂– groups.

Based on the above results, it appears that the ring structures and islands ('dots') are formed on an underlying layer of the dendrimers physisorbed on mica. Preliminary results also indicated the absence of ring structures at a monolayer coverage.[†] During spin coating, when the liquid film of the excess dendrimers and the solvent (THF) on top of the

monolayer thins below a critical thickness by evaporation, the instability of the film may cause film rupture into small droplets.³ Some of the small droplets coalesce into larger ones, and the remaining isolated small droplets dry to form the observed islands ('dots'). AFM imaging of freshly prepared films showed that the rings were developed from larger droplets,[†] in agreement with the mechanism proposed by others.³ The process involves a radial flow outward from the center of the droplet.^{3,11} This outward flow of liquid can carry virtually all of the dissolved dendrimers as well as some of the dendrimers physisorbed on the substrate surface to the rim. The reduced number of dendrimers in the layer on the interior of the ring then flatten to cover the substrate surface. The observed similar heights and widths of the rims regardless of the ring diameters might be required for 'pinning' of the rim.⁵

In conclusion, we have described the preparation of robust submicrometer ring structures on mica surfaces using **1**. AFM studies revealed that the isolated mesoscopic ring structures and islands were grown on an underlying self-assembled layer of the dendrimers. The surface inside the rings is much flatter than outside. Prior to curing, polymerization of the hydrolyzed dendrimers, if any, occurred only to a limited extent. Scanning probe lithography of the pre-cured films can be used to generate patterns (*e.g.* Fig. 3) on the film.¹² The structures become robust upon curing. Similar to the demonstrated application of graphite etch pits (3.5 Å high),¹³ such ring structures (*ca.* 50 Å high) may be used to isolate ensembles of macromolecules or nanoparticles for study by scanning probe microscopy. We will explore the growth of ring structures using analogs of **1** that possess functional groups at the phenyl group.

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Notes and references

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