Supplementary Material (ESI) for Chemical Communications

Nano-Patterning of Solid Substrates by Adsorbed Dendrimers

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Optical Reflectometry

The adsorption of PAMAM dendrimers has been studied by means of in-situ optical reflectometry, commonly known as poorman's reflectometry. A polarized laser beam is reflected at an interface and is subsequently separated into its parallel (p) and perpendicular (s) polarizations using a polarizing beam splitter and the intensity of these two polarizations are detected separately as I_p and I_s respectively. The adsorbed mass Γ is obtained from

$$\Gamma = \frac{1}{A_s}\frac{S - S_0}{S_0}$$

where is given by $S = I_p / I_s$ and S_0 is the value of S prior to adsorption and $A_s \approx 0.013$ m^2/mg is a sensitivity factor calculated for each experiment on the basis of an optical model. The adsorbed mass is converted into surface coverage θ by making use of

$$\theta = \frac{\Gamma N_A}{M}\pi a^2$$

where N_a is Avogadro's number, M is the molecular mass, and a is the radius of the adsorbed dendrimers as measured by atomic force microscopy (see below).

The substrates are polished silicon wafers (p-type, boron doped) from Silchem GmbH were oxidized thermally in a furnace at 1000° C for 75 minutes. This procedure results in a SiO_2 layer of about 90 nm in thickness, as determined in air with a null ellipsometer (Optrel, Germany). The oxidized wafers are then cut into samples with a width of around 12 mm. Cleaning was performed in a mixture of 24% NaOH, 30% H_2O_2, and Millipore water in a ratio of 1:1:5, by volume at 75° C for 10 minutes. Prior to experiments, the substrate is rinsed profusely with water and subsequently dried in a stream of pure nitrogen. Reflectometry measurements are carried out in a home-built reflectometer with an impinging jet cell at a wavelength of 633 nm and an angle of incidence of 45° relative to the surface of the prism, such that the angle of incidence at the surface of adsorption is around 54°. The setup is similar as the one used was described by J. C. Dijt et al., Adv. Colloid Interface Sci., **1994**, 50, 79-101. The cell has a bore of 1.0 mm in diameter, a separation distance of 0.85 mm and a flow rate of 0.5-1 mL/min was used. Initially the interface is flushed with the pure electrolyte solution, and then the feed is switched to a solution of PAMAM dendrimers of a concentration of 5.94 mg/L.

Figure S1 shows a typical set of reflectometry results. The initial rise is in good agreement with fast deposition based on a perfect sink model. The subsequent adsorption plateau corresponds to the saturated surface, from which the maximum coverage was determined.

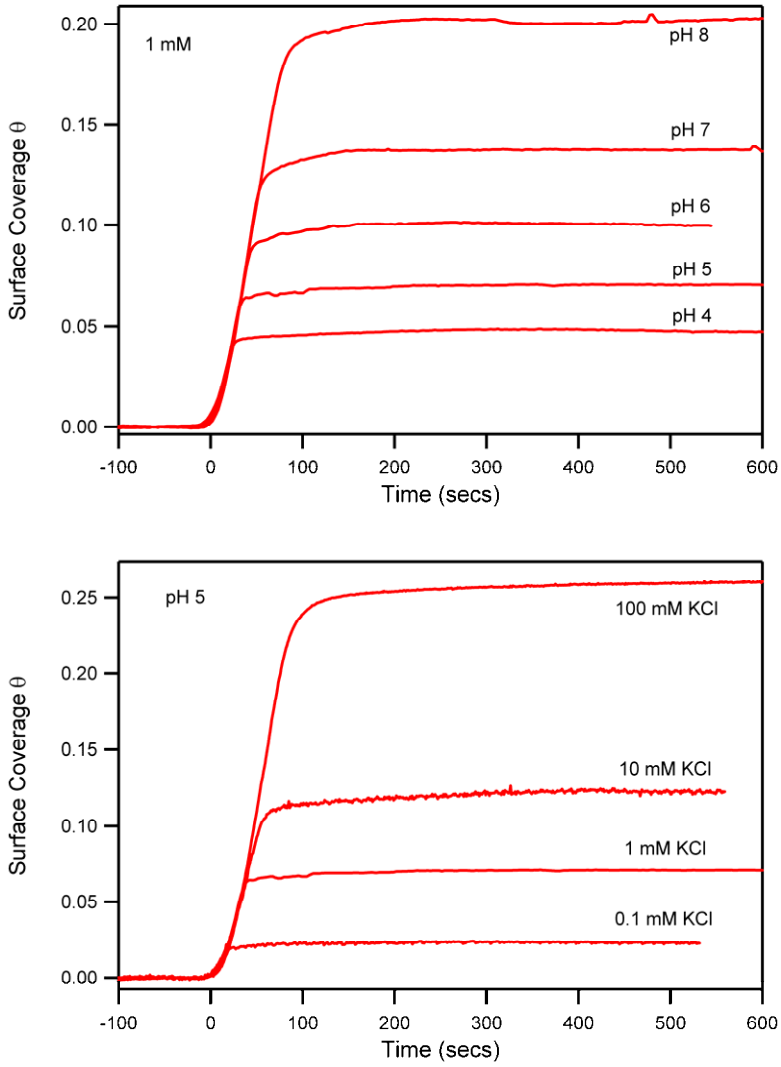

Figure S1. Time dependence of the adsorbed coverage of G10 PAMAM dendrimers on a silica surface measured with in situ reflectometry. The upper graph shows the effect of pH at 1 mM ionic strength in KCl, while the lower graph shows the effect of ionic strength at pH 5.

AFM imaging

The structure of the adsorbed dendrimer layers is determined by AFM-imaging with tapping mode in air (Multimode Nanoscope III, Veeco, CA). The substrates were rinsed with deionised water and dried in air. The number density of adsorbed dendrimers is estimated from 1×1 μm scans taken at least 5 different positions, whereby 500-1500 dendrimers have been counted. For these measurements standard tapping mode cantilevers are used, while for the determination of the geometrical dimensions of the dendrimers cantilevers with small tip radii below 5 nm are employed. The correction due to the finite radius of the AFM-tip is performed on the raw images with the program Deconvo 1.1 (Silicon MDT Ltd, Russia). The radii of the adsorbed dendrimers are obtained by an image analysis program under IGOR PRO (WaveMetrics, OR) based on the algorithm proposed by S. Barrett et al, J. Comp. Assist. Microscopy, **1998**, 10, 77. The resulting geometrical dimensions of the PAMAM dendrimers on silica are given in the table below. One observes that the dendrimers flatten on the surface and that their height is about 20-25% of their diameter.

	Radius in solution (nm)[a]	Radius in adsorbed state (nm)[b]	Height in adsorbed state (nm)[b]
G10	6.7	8.4 ± 1.3	4.0 ± 0.9
G8	4.9	5.0 ± 1.6	2.0 ± 0.7

[a]From light scattering as provided by the manufacturer (Dendritech).
[b]From present AFM investigations.

In order to exclude artefacts due to different adsorption conditions, certain samples were prepared under absolutely identical conditions for both substrates. In particular, several samples are immersed simultaneously in a given solution for the same duration of 12 h. They are rinsed thereafter and dried. Figure 2 shows AFM-images from such experiments. These experiments clearly confirm the important role of the substrate. For silica, the coverage obtained by reflectometry and AFM are in good agreement.

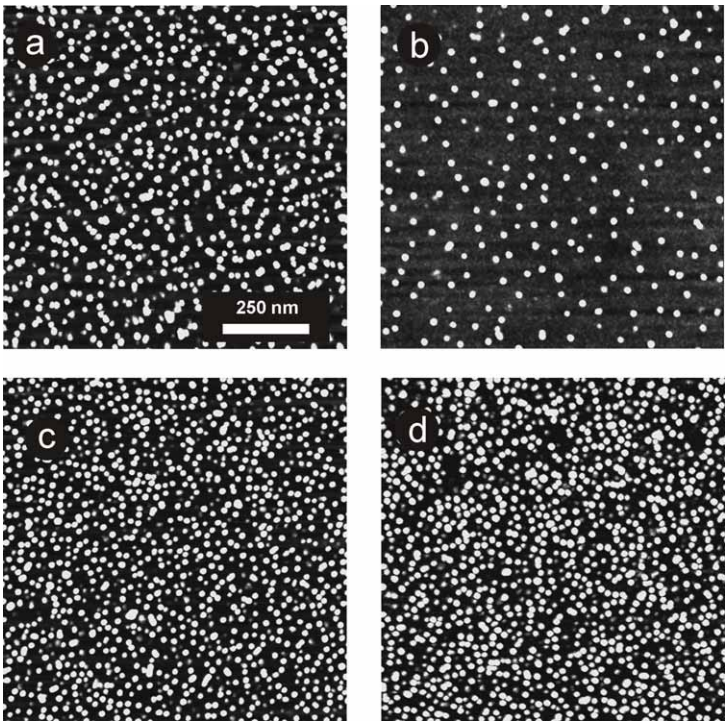

Figure S2. PAMAM G10 dendrimers adsorbed at pH 4 to mica (left column, a, c) and silica (right column, b, d) under identical conditions. The measurements are done at two different ionic strengths 0.5 mM (top row, a, b) and 40 mM (bottom row, c, d).