COMMUNICATIONS

## Surface-Confined Metallodendrimers: Isolated Nanosize Molecules**

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Current technology allows the patterning of surfaces at the submicrometer level but there is a considerable tendency to decrease this to the nanometer level.[1] Nanotechnology aims at the design and manufacture of nanosize devices,[2] and ultimately the components may consist of single molecules. However, there are two minimal requirements that need to be fulfilled: the simple synthesis of functional nanosize structures and the controlled positioning of these molecules. Dendrimers are a class of molecules of nanometer-size dimensions and they can be synthesized in a limited number of steps. They have a well-defined treelike architecture, and a wide variety of dendrimers with various cores, monomeric units, and functional groups have been reported.[3, 4] Self-assembly, in particular self-assembly of sulfur-containing compounds on gold surfaces, is a versatile method to order and orient molecules at an interface.[5, 6] Scanning tunneling microscopy (STM) showed that individual thiols can be isolated by insertion into a dodecanethiol monolayer on a gold surface.[7] Therefore, modification of a gold surface by the self-assembly of dendrimers seems to be a promising strategy to achieve surface-confined nanosize structures. Only a few studies have addressed dendrimers in spin-cast films.[8] Spontaneous surface confinement has been achieved by Crooks et al., who attached dendrimers to gold surfaces through the dendrimer end groups.[9, 10]

Our strategy to construct structures with nanometer dimensions relies on the self-assembly of specifically designed dendritic wedges that are easy to synthesize and to functionalize. Potentially, they can be chemically modified after surface confinement. The dendritic wedges are prepared by noncovalent synthesis, analogous to the controlled assembly of metallodendrimers previously developed in our group.[11]

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A dendritic wedge was grown from a sulfide-derived core (→**MG$_0$**) for the attachment of metallodendrimers to the gold surface. Sulfide **2** was prepared by reaction of 11-bromo-1-undecene (**1**)[12] with 9-borabicyclo[3.3.1]nonane (9-BBN) and 1-decanethiol (Scheme 1). The ^{1}H NMR spectrum of **2**
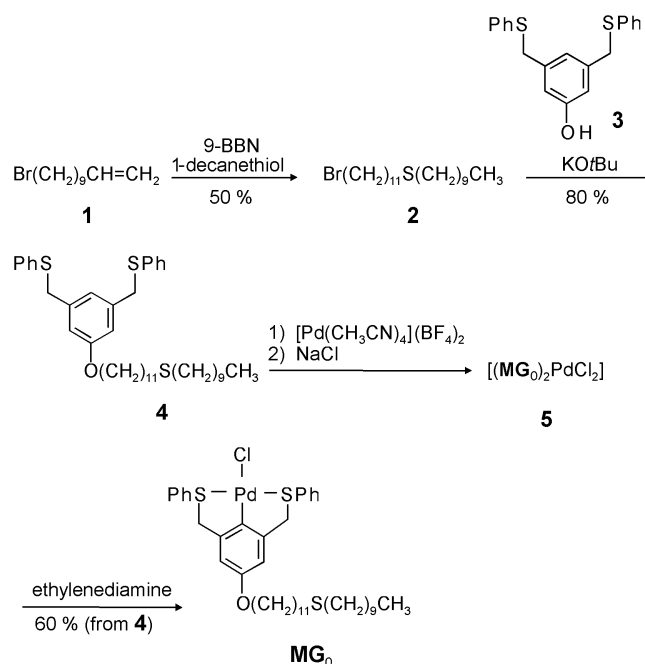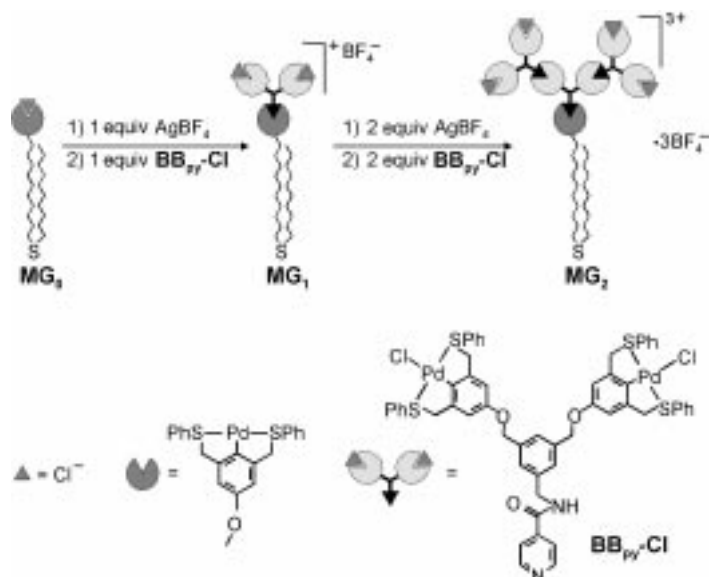

Scheme 1. Synthesis of the dendrimer core.

showed the complete conversion of the double bond. The pincer ligand was introduced by reaction of **2** with **3**[13] in the presence of a base. Ligand **4** was subsequently treated with two equivalents of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ and converted into the overall neutral Pd-Cl complex by stirring with aqueous NaCl. More than one equivalent of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ is needed for complete cyclopalladation, because the sulfide in the long alkyl chain also forms a complex with the Pd^{II} reagent. Initially, the trinuclear complex **5** was formed, which was isolated and subsequently converted into **MG$_0$** by addition of the chelating ethylenediamine. Formation of **MG$_0$** was confirmed by an intense signal at $m/z = 769.2$ ([$M^+ - Cl$], calcd: 769.3) in the FAB-MS spectrum.

Higher generation metallodendritic wedges with a sulfide chain were synthesized by controlled assembly. **MG$_0$** was activated by reaction with one equivalent of AgBF$_4$ and subsequently one equivalent of **BB$_{py}$-Cl**[14] was added (Scheme 2). This complex coordinates to the palladium center through the pyridine moiety. The first generation dendrimer (**MG$_1$**) was formed in essentially quantitative yield. This procedure was repeated with **MG$_1$** and two equivalents each of AgBF$_4$ and **BB$_{py}$-Cl** to afford the second-generation dendrimer **MG$_2$**. The ^{1}H NMR spectra of both **MG$_1$** and **MG$_2$** clearly reflected the coordination of the pyridine ligands with a shift of the α-pyridine protons from $\delta = 8.54$ to $\delta = 8.30$, similar to the previously reported metallodendrimer synthesis.[14] The successful formation of the dendritic assemblies was further confirmed by the presence of the molecular peaks minus a BF$_4^-$ counter ion at $m/z = 1962.0$ (calcd: 1961.3) and

Scheme 2. Controlled assembly of dendrimers.

Figure 1. AFM height image (tapping mode) of the [D_{21}]decanethiol monolayer on Au(111) after treatment with a solution of a) metallodendrimer **MG₂** and b) reference compound (**G₂ₚᵧ**). (Color scale from dark to white: $Z = 10$ nm).

4461.3 (calcd: 4458.2) for **MG₁** and **MG₂**, respectively, in the MALDI-TOF mass spectra.[15]

Gold [Au(111)] substrates covered with a [D_{21}]decanethiol monolayer (five hours immersion time in a 1 mm ethanol solution) were placed in a nitromethane/dichloromethane solution (ca. 2/1) of these dendritic sulfide adsorbates **MG₁** and **MG₂**, respectively. The adsorption time was varied from 30 min to 20 h. All layers were characterized with contact angle measurements, secondary ion mass spectrometry (SIMS), and atomic force microscopy (AFM).[16] Incorporation of the dendrimers resulted in a distinct decrease in the contact angles (advancing and receding) as a function of the exchange time. The decrease of the advancing contact angle indicates a more hydrophilic surface, which is consistent with the introduction of polar compounds. The decreased receding contact angle indicates a rougher surface, which is as expected. It takes five hours for the contact angles to decrease from 105°/95° to 70°/18°,[17] which indicates that the adsorption is a slow process. The presence of the dendrimer adsorbates was confirmed by SIMS experiments; a characteristic fragmentation pattern of the palladium pincer ligand was detected around $m/z = 442 – 447$ ([$C_{20}H_{16}OS_2Pd$]⁺; calcd: 442.9). The same fragments are present in the MALDI-TOF mass spectrum of bulk **MG₂**.

The decanethiol monolayer samples in which the adsorbed dendrimers are incorporated were further characterized by means of AFM in contact mode in water or ethanol and in tapping mode in air. Figure 1a shows a tapping-mode AFM image of the alkanethiol monolayer after 2.5 h contact with a solution of the dendrimer **MG₂** (5×10^{-5} m in CH_3NO_2/CH_2Cl_2, 1/1). The image exhibits distinct features with nanometer dimensions that do not change position upon scanning in tapping or in contact mode. The sizes of these dendrimers were measured on different samples with the same AFM tip (**MG₁** height 0.6 ± 0.2 nm, width 20 ± 4 nm; **MG₂** height 0.9 ± 0.2 nm, width 23 ± 4 nm). On average the features from a solution of **MG₁** are smaller than the features from a solution of **MG₂**. The height of the adsorbed
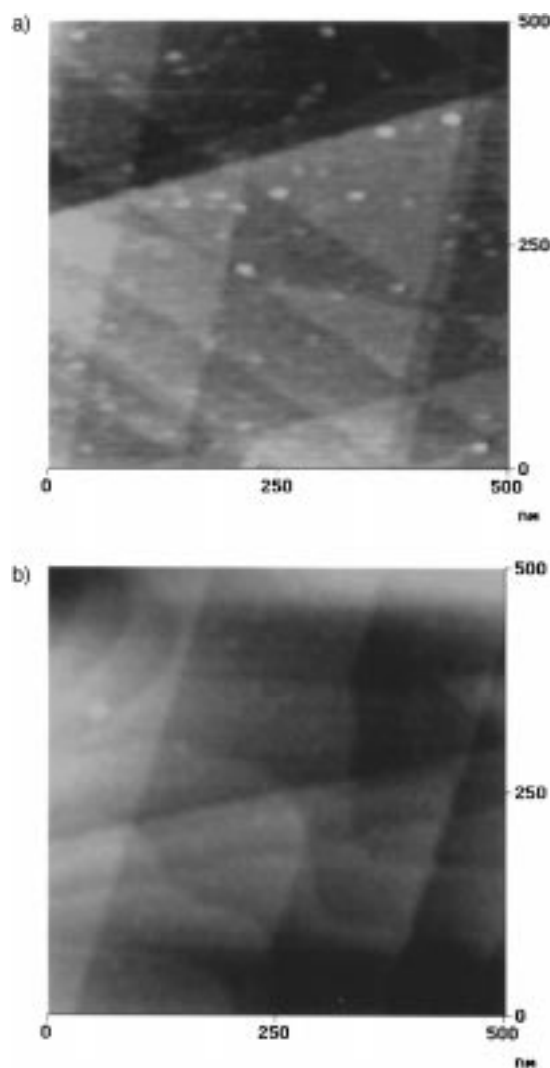
dendrimers in the tapping-mode AFM images matches the expected size calculated from CPK models of the dendrimer adsorbate. Nevertheless, the absolute value of the height can deviate from this value when the interaction between the AFM tip and the dendrimer is significantly different from the interaction of the tip with the surrounding alkanethiol monolayer.[18] However, with the very soft tapping conditions employed in our experiments these values can be regarded as a good representation of the feature height.[19] Furthermore, the observed height difference between **MG₁** and **MG₂** is consistent with the expected increase in size, when it is assumed that the dendrimer part lies as a flat disc on the surface. The width of the features as determined with AFM depends on the radius of the tip.[20] By considering the observed feature heights we can safely arrive at the conclusion that the particle widths are smaller than the characteristic tip radius.

The concentration of these dendrimer adsorbates on the surface was determined from the AFM images by counting the number of particles in a square of 200×200 nm² on a flat

terrace. The number of dendrimers on the surface increased with time and seems to level off (Figure 2). After 20 h the surface concentration is approximately 55 dendrimers per 200×200 nm^2, which corresponds to a surface coverage of roughly 1%.

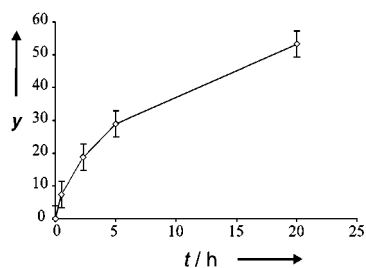Figure 2. Number of metallodendrimers on a decanethiol monolayer as a function of the time in a **MG$_2$** solution as determined with AFM (tapping mode). y = number of dendrimers per 200×200 nm^2.

To achieve insight into the specificity of the binding of the dendrimer two control experiments were performed with slightly modified compounds, that is, a second generation dendrimer without sulfide chain (**G$_{2,py}$**)[14] and with a dendrimer in which the sulfide chain is replaced by an alkyl chain (**MG$_{2,C22}$**). These compounds do not bind to the substrate at all (Figure 1 b), which strongly indicates that **MG$_1$** and **MG$_2$** bind to the gold substrate through the sulfide moiety (Figure 3).
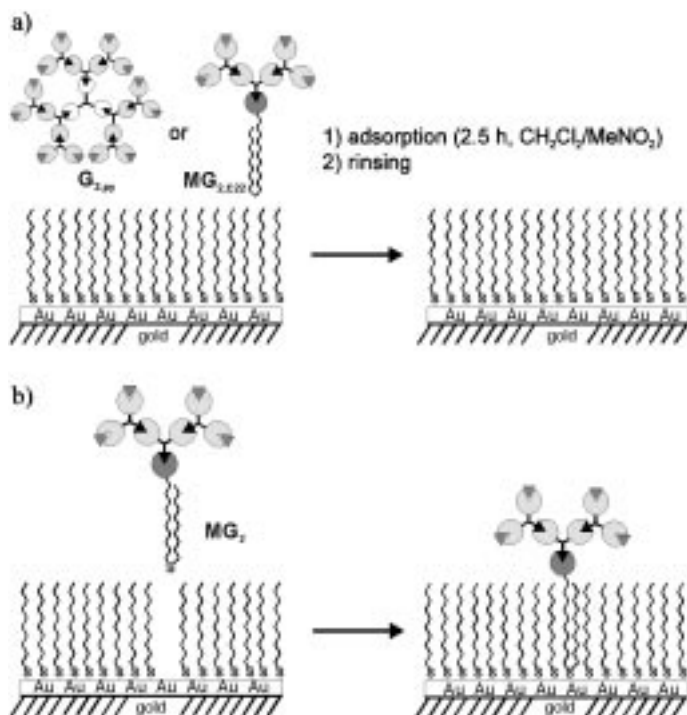

Figure 3. Schematic representation of the interaction of metallodendrimers in an alkanethiol monolayer. a) Control experiments with reference compounds without sulfide groups showed no binding to the substrate. b) The metallodendrimer **MG$_2$** binds through its dialkyl sulfide group at a defect site in the alkanethiol monolayer.

In regard to the mechanism of the binding of the dendrimer adsorbate to the substrate it is important to note that both AFM and wetting experiments show that it is a relatively slow

process (hours). Therefore, binding of the dendrimers is not simply a physisorption on the monolayer or substrate.[21] Since the reference dendrimers without a sulfide moiety are not incorporated in the monolayer binding must occur through the dialkyl sulfide group. Defects in the alkanethiol monolayer, either present after the alkanethiol monolayer preparation or formed during the exchange experiment, are required for binding of the sulfide to the gold substrate.[22] Consequently, the rate of the adsorption process of the dendrimer adsorbates can be limited by the insertion of the dialkyl sulfide moiety, or by the formation of defect sites. In an effort to distinguish between these two options the rate of formation of defect sites was monitored by measuring the electrochemical resistance. The monolayer resistance can be measured accurately and is very sensitive to the number of defects.[23] The resistance was determined after leaving the alkanethiol monolayer in contact with the solvent (dichloromethane/nitromethane, 1/1) for 2.5 h in the absence of the dendrimer adsorbate. This resulted in a sharp decrease in the resistance of the monolayer. However, nearly all of the monolayer is still present as evident from an increase in the capacitance of the layer from 1.5 µF cm^{-2} to only 3.6 µF cm^{-2}.[24] The capacitance of bare gold under our conditions is 45–50 µF cm^{-2}. These values lead to a surface coverage of roughly 96%. This value is somewhat smaller than estimated from the surface densities of adsorbed dendrimers and might indicate that defects are present in the thiol monolayer that are not accessible to or not yet filled by the dendrimer adsorbate. These results are, however, in full agreement with partial monolayer desorption and subsequent adsorption of the dendrimers at defects in the monolayer. As the timescale of the defect formation in the control experiment is approximately the same as the increase of the dendrimer surface concentration, it is likely that the formation of the defects in the monolayer is the rate-limiting step. The initial quality, that is, the packing, of the thiol monolayer is an important parameter for dendrimer adsorbate incorporation. The number of incorporated dendrimer wedges decreased with increased immersion time (4 min, 5–8 h, and 16 h) of the gold substrate in a 1 mM solution of the thiol in ethanol. This shows that less defects are present and/or are formed upon solvent exposure in more densely packed thiol monolayers.

In conclusion, we have shown that metallodendrimers with sulfide side chains can be inserted as individual particles in an alkanethiol monolayer and that the number of isolated dendrimers can be controlled with time. The alkanethiol partly desorbs from the gold surface and the dialkyl sulfide-derived metallodendrimers adsorb at these defect sites. In order to achieve true "nanofabrication" the control over the number of dendrimers must be extended to a control over the positioning of the particles. In addition, we aim to chemically modify such individual assemblies.

Experimental Section

4: KO*t*Bu (1.0 g, 9.0 mmol) was added to a solution of **3** (1.0 g, 3.0 mmol) in THF (50 mL), and the mixture was stirred at room temperature for 1 h. Subsequently, bromide **2** (1.2 g, 3.0 mmol) was added and the reaction mixture was stirred overnight. After removal of the solvent the residue was

dissolved in CH_2Cl_2 (50 mL) and the organic layer was washed with 1N HCl (50 mL), saturated $NaHCO_3$ solution (50 mL), and brine. After drying the solution on $MgSO_4$ and concentrating under reduced pressure, pure ligand **4** was obtained as a colorless oil by column chromatography (silica gel, CH_2Cl_2). Yield 1.6 g (80 %). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.34 – 7.16$ (m, 10H; SPh), 6.82 (s, 1H; ArH), 6.71 (s, 2H; ArH), 4.03 (s, 4H; Ar-CH_2S), 3.88 (t, $^3J = 7.4$ Hz, 2H; CH_2O), 2.50 (t, $^3J = 7.3$ Hz, 4H; CH_2SCH_2), 1.80–1.60 (m, 2H; CH_2CH_2O), 1.60–1.40 (m, 4H; CH_2CH_2SCH_2CH_2), 1.40–1.20 (m, 28H; CH_2), 0.91 (t, $^3J = 6.6$ Hz, 3H; CH_3); FAB-MS (m-nitrobenzyl alcohol (NBA)): m/z: 664.4 $[M^+]$, calcd for $C_{41}H_{60}OS_3$: 664.4).

MG$_0$: Two equivalents of $[Pd(CH_3CN)_4(BF_4)_2]$ (0.66 g, 1.50 mmol) were added to a solution of ligand **4** (0.50 g, 0.75 mmol) in CH_3CN (50 mL). A color change from bright orange to dark yellow indicated cyclopalladation and after stirring the mixture for 1 h at room temperature the solvent was evaporated in vacuo. The residue was dissolved in a mixture of CH_3CN/CH_2Cl_2 (1/1, 50 mL) and stirred vigorously with brine (50 mL) for 24 h. After separating the layers, the organic layer was washed with an aqueous solution of ethylenediamine. Subsequently, the organic solvent was evaporated and the remaining solid purified by column chromatography (silica gel, CH_2Cl_2) to give 0.60 g (60 %) of **MG$_0$** as a yellow solid. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.80 – 7.75$ (m, 4H; SPh), 7.37 – 7.30 (m, 6H; SPh), 6.51 (s, 2H; Ar$_{Pd}$-H), 4.48 (br s, 4H; CH_2S), 3.85 (t, $^3J = 7.4$ Hz, 2H; OCH_2), 2.50 (t, $^3J = 7.3$ Hz, 4H; CH_2SCH_2), 1.80–1.60 (m, 2H; OCH_2CH_2), 1.60–1.50 (m, 4H; CH_2CH_2SCH_2CH_2), 1.50–1.20 (m, 28H; CH_2), 0.90 (t, $^3J = 6.6$ Hz, 3H; CH_3); EI-MS: m/z: 769.2 ($[M^+ - Cl]$, calcd for $C_{41}H_{59}OS_3Pd$: 769.3). Elemental analysis calcd for $C_{41}H_{59}ClOPdS_3$: C 61.10, H 7.38, Cl 4.40, S 11.93, Pd 13.20; found: C 60.86, H 7.23, Cl 4.38, S 11.88, Pd 12.96.

MG$_1$: A freshly prepared stock solution of AgBF$_4$ (175 μL, 21 μmol) in water (120 mm) was added to a solution of **MG$_0$** (16.2 mg, 21 μmol) in CH_2Cl_2/CH_3CN (5/1, 5 mL). The mixture was stirred for 5 min and the color changed from bright to pale yellow. Subsequently, a solution of **BB$_{pyr}$-Cl** (24.8 mg, 21 μmol) in CH_2Cl_2 (2 mL) was added. The mixture was stirred for 5 min, followed by evaporation of the solvent under reduced pressure. The residue was dissolved in CH_2Cl_2/$MeNO_2$ (1/1, 10 mL), after which the solvent was evaporated. This was repeated twice. Finally, the residue was partly dissolved under heating to 60 °C in CH_2Cl_2/$MeNO_2$ (1/1, 10 mL) and filtered to remove AgCl. After evaporation of the organic solvents **MG$_1$** was obtained as a yellow solid (28 mg, 75 %). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.25$ (br s, 2H; Pyr-H$_\alpha$), 7.80 (br s, 12H; SPh), 7.60 (br s, 2H; Pyr-H$_\beta$), 7.50–7.33 (m, 21H; SPh+ArH), 6.70 (br s, 6H; Ar$_{Pd}$-H), 5.00 (br s, 4H; CH_2O), 4.85–4.40 (m, 14H; ArCH_2S+CH_2N), 3.90 (br s, 2H; OCH_2), 2.40 (br s, 4H; CH_2SCH_2), 1.80–1.60 (br s, 2H; OCH_2CH_2), 1.55–1.00 (m, 32H; CH_2), 0.90 (br s, 3H; CH_3); MALDI-TOF MS (matrix 1):[14] m/z: 1962.0 ($[M - BF_4]^+$, calcd for $C_{96}H_{105}O_4S_7N_2Pd_3Cl_2$: 1961.3).

MG$_2$: **MG$_1$** was synthesized from **MG$_0$** (4.8 mg, 6 μmol) with adjusted amounts. Subsequently, **MG$_2$** was assembled analogously from **MG$_1$** with AgBF$_4$ (100 μL, 12 μmol) and **BB$_{pyr}$-Cl** (14.4 mg, 12 μmol). **MG$_2$** was obtained as a yellow solid (18 mg, 66 %). ^1H NMR (250 MHz, $CDCl_3$/CD_3NO_2, 1/1): $\delta = 8.25$ (br s, 6H; Pyr-H$_\alpha$), 7.80 (br s, 42H; SPh), 7.60 (br s, 6H; Pyr-H$_\beta$), 7.50–7.33 (m, 37H; SPh+ArH), 6.70 (br s, 14H; Ar$_{Pd}$-H), 5.00 (br s, 12H; CH_2O), 4.85–4.40 (m, 34H; CH_2S+CH_2N), 3.90 (br s, 2H; OCH_2), 2.40 (br s, 4H; CH_2SCH_2), 1.70 (br s, 2H; OCH_2CH_2), 1.55–1.00 (m, 32H; CH_2), 0.90 (br s, 3H; CH_3); MALDI-TOF MS (matrix 1):[14] m/z: 4461.3 ($[M - BF_4^-]^+$, calcd for $C_{206}H_{197}N_6O_{10}S_{15}Pd_7Cl_4B_2F_8$: 4458.2).

Atomic force microscopy: The AFM measurements were performed with a NanoScope III Multimode instrument (Digital Instruments, Santa Barbara, CA, USA). AFM images (Tapping mode) were acquired with silicon cantilevers/tips (Digital Instruments) in air (cantilever resonance frequency $f_0 = 280 – 320$ Hz). The setpoint was adjusted to 0.90–0.95.

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