Patterned, Hybrid, Multilayer Nanostructures Based on Multivalent Supramolecular Interactions

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Various patterning strategies have been developed to create hybrid nanostructures of dendrimers and gold nanoparticles on cyclodextrin self-assembled monolayers (CD SAMs) based on multiple supramolecular interactions using a layer-by-layer (LBL) approach. A lack of specificity of the adsorption of the dendrimer prevented the use of LBL assembly on chemically patterned SAMs, which were prepared by microcontact printing (μCP) or nanoimprint lithography (NIL). Nanotransfer printing (nTP) and nanoimprint lithography solved that problem and resulted in patterned LBL assemblies on the CD SAMs. nTP was achieved by LBL assembly on a PDMS stamp followed by transfer onto a full CD SAM. NIL-prepared PMMA patterns provided patterned CD SAMs and functioned as a physical mask for LBL assembly. For these methods, differences in thickness of the LBL assemblies were observed when compared to LBL assembly on full CD SAMs. These differences were shown not to originate from rinsing or lift-off procedures, but probably from differences in wetting.

Introduction

Nanotechnology requires new methodologies for the assembly of molecular- to micrometer-scale objects onto substrates in predetermined arrangements for the productivity of sensors, electrical and optical devices, MEMS, and photonic systems.[1] The ability to achieve control over the lateral dimensions, deposit films of different compositions onto a surface, and to construct 3D devices is important for such methodologies.[2]

Layer-by-layer (LBL) assembly[3] is a simple and elegant method for fabricating structured and functional thin films on solid substrates. The technique is based on the sequential adsorption of species with complementary affinities on a substrate of arbitrary composition or topology. It allows buildup of films with nanometer thickness control.[3,4] LBL structures can contain various structural entities from conducting and dielectric layers to functional organic and inorganic nanoparticles. LBL assembly is therefore emerging as an inexpensive and versatile technique to create electro-optical,[5] conducting,[6] and luminescent[7] thin films and to provide functional systems for photovoltaics,[8] cell templating,[9] and drug delivery.[10]

Achieving high spatial resolution while retaining the interfacial properties and specificity of the components is a key issue. Hammond and co-workers introduced a route to pattern polymeric films by using chemically patterned surfaces as templates for electrostatic LBL assembly.[11] Patterning of full multilayers using UV or thermal cross-linking followed by dissolution of the non-cross-linked areas has been developed as well, but it requires the introduction

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of a photo-cross-linkable monomer into the LBL assembly.[12] Cui and co-workers described a metal mask and liftoff approach to pattern LBL assemblies of two different types of nanoparticles.[13] Polymer-on-polymer stamping (POPS)[14] has been used to create a pattern of a single layer of chemical functionality on top of an existing multilayer. Additionally, Park and Hammond performed LBL assembly on a PDMS relief stamp, which allowed subsequent transfer of the LBL structures onto a substrate in the contact areas.[15] This approach resembles nanotransfer printing (nTP), which was developed by Rogers and co-workers.[16] Furthermore, Hammond's group introduced the use of UV-curable material as a mold in contact printing processes and imprint lithography and applied it to the so-called polymer transfer printing[17] to achieve a chemically patterned monolayer on multilayer assemblies, in the sub-micrometer range down to 80 nm.[18]

We have reported cyclodextrin (CD) self-assembled monolayers (SAMs) on gold[19] and silicon oxide[20] surfaces on which molecules can be positioned by means of multiple supramolecular interactions. Therefore, these CD SAMs constitute molecular printboards onto which molecules,[21,22] supramolecular assemblies,[23] and nanoparticles[24] can be immobilized. We have also described the LBL assembly on full CD SAMs of hybrid organic/metal nanoparticle multilayers using multivalent supramolecular interactions between dendritic guest molecules and CD-modified gold nanoparticles.[25] These multilayers showed a well-defined thickness control of 2 nm per bilayer.[25]

In the present study, we have compared various other methods to create patterns of these supramolecular LBL assemblies. Microcontact printing (μCP) and nanoimprint lithography (NIL) have been used to create patterned SAMs to obtain directed LBL assembly, nTP has been employed to transfer complete LBL assemblies, and NIL has provided topographical masks for LBL assembly. Emphasis lies on the interfacial supramolecular specificity and on the layer growth characteristics.

Experimental Section

Materials. Chemicals were obtained from commercial sources and used as such. β-Cyclodextrin (CD) was dried in a vacuum at 80 °C in the presence of P_2O_5 for at least 5 h before use. Solvents were purified according to standard laboratory methods.[26] *per*-6-Thio-β-cyclodextrin[27] and *per*-6-amino-β-cyclodextrin[28] were synthesized according to literature procedures. Milli-Q water with a resistivity >18 MΩ·cm was used in all experiments. Generation 5 adamantyl-terminated poly(propylene imine) (PPI) dendrimers (with 64 adamantyl groups) were synthesized as reported before.[29] Synthesis of the β-cyclodextrin heptathioether adsorbate was reported previously.[19] 1-Mercapto-11-undecyl-tetra(ethylene glycol) ($HS-(CH_2)_{11}-(EG)_4OH$) was synthesized according to a literature procedure.[30] Cyclodextrin-functionalized gold nanoparticles were synthesized according to a literature procedure,[31] by the reduction of $HAuCl_4$ in DMSO by $NaBH_4$ in the presence of *per*-6-thiocyclodextrin. Using TEM, a mean particle size of 2.8 ± 0.6 nm was found.[32]

Substrate Preparation. All glassware used to prepare monolayers was immersed in piraña (concentrated H_2SO_4 and 33% H_2O_2 in a 3:1 ratio). (Warning! piraña should be handled with caution; it has detonated unexpectedly.) The glassware was rinsed with large amounts of Milli-Q water. All adsorbate solutions were prepared freshly prior to use. Gold substrates for AFM (20 nm of gold on a glass substrate) were obtained from Ssens BV (Hengelo, The Netherlands). Prior to use the substrates were cut to the preferred shape and size.

Microcontact Printing (μCP). Gold substrates were cleaned by immersing the substrates in piraña for 5 s and leaving the substrates for 5 min in absolute EtOH.[33] Stamps were fabricated by casting a 10:1 (v/v) mixture of PDMS and curing agent (Sylgard 184, Dow Corning) against a photolithographically patterned silicon master, cured for 1 h at 60 °C, and released at this curing temperature. PDMS stamps were left in the oven at 60 °C for at least 18 h to ensure complete curing. For the μCP-patterned SAMs, microcontact printing of an inert SAM (1-mercaptoundec-11-yl-tetra(ethylene glycol) or 11-mercaptoundecanol) onto a gold surface was performed by inking the PDMS stamps with a 1 mM adsorbate in ethanol solution for 15 min. After removal from the solution and drying under a flow of nitrogen, the stamps were applied by hand for 1−2 min onto the clean gold substrate. The substrates were rinsed with Milli-Q water and dried under a flow of nitrogen. The patterned substrates were subsequently immersed into a 0.1 mM β-CD heptathioether adsorbate solution in EtOH and $CHCl_3$ (1:2

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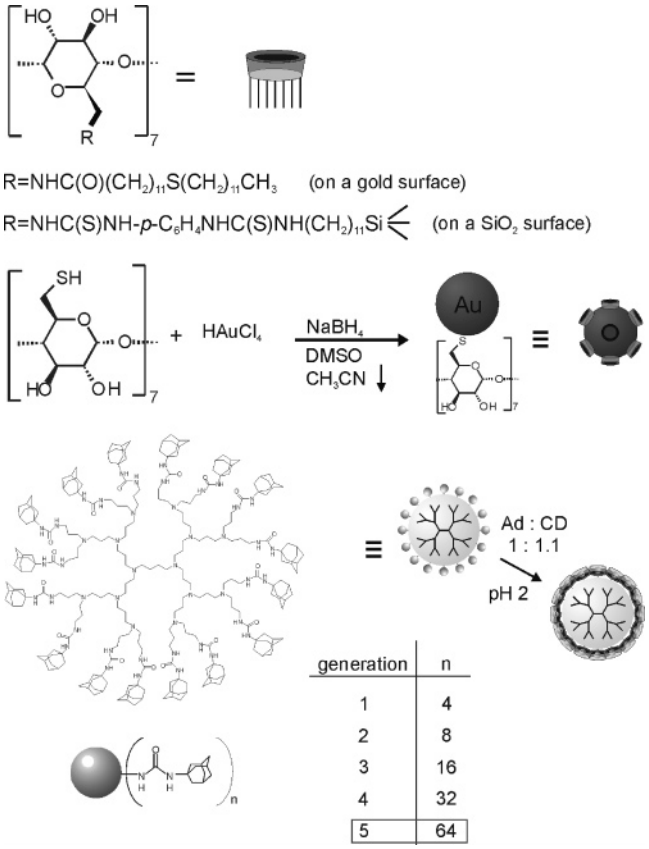
v/v) for 16 h at 60 °C. For nTP, substrates were subsequently immersed into a 0.1 mM β-CD heptathioether adsorbate solution in EtOH and $CHCl_3$ (1:2 v/v) for 16 h at 60 °C. The samples were removed from the solution and rinsed with substantial amounts of chloroform, ethanol, and Milli-Q water. Oxidation of the PDMS stamps was carried out in a commercial UV/ozone plasma reactor (UltraViolets Product Inc., model PR-100) for 30 min. The PDMS stamps were kept hydrophilic by immersing the stamps in an aqueous ink solution immediately after UVO treatment. After multilayer formation, the stamps were applied by hand for 5 min onto the CD SAM. At last, the substrates were thoroughly rinsed with large amounts of an aqueous solution of 10 mM native β-CD followed by Milli-Q water. Substrates were dried under a flow of nitrogen.

Nanoimprint Lithography (NIL). Stamps for NIL were made by photolithography followed by reactive ion etching (RIE, Elektrotech Twin system PF 340). 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane was used as an anti-adherent layer to facilitate the stamp−imprint separation. Silicon oxide substrates were first oxidized by immersion in piraña solution for 15 min and then covered with a 400 nm thick layer of PMMA by spin-coating. Stamp and substrate were put in contact and a pressure of 40 bar was applied at a temperature of 180 °C using a hydraulic press (Specac). The residual layer was removed by dipping the samples in acetone for 60 s.[34] For the NIL-patterned SAMs, a 20 nm layer of gold was evaporated using a metal evaporator BAK 600 at a vacuum of 1×10^{-6} mbar. The metal liftoff was achieved using acetone and ultrasonication. After metal liftoff, assembly of an inert SAM (*n*-(3-trimethoxysilylpropyl)-ethylenediamine or 2-[methoxy-poly(ethyleneoxy)-propyl]trimethoxysilane (6−9 ethylene glycol units per molecule)) onto the silicon oxide surface was performed by gas-phase evaporation as described before,[34] or the silica oxide surface was left unfunctionalized. The NIL-patterned substrates were subsequently immersed into a 0.1 mM β-CD heptathioether adsorbate solution in EtOH and $CHCl_3$ (1:2 v/v) for 16 h at 60 °C. NIL-patterned CD monolayers in PMMA structures were prepared following a procedure similar to the one described by Onclin et al.,[20] although some changes were done in order to maintain the PMMA structures:[35] After aminoalkyl SAM formation from the gas phase, the diisocyanate was reacted in ethanol (40 °C, 2 h), and the CD heptamine was subsequently reacted in water (40 °C, 2 h).

Layer-by-Layer (LBL) Assembly. μCP-patterned CD SAMs, NIL-patterned CD SAMs, and NIL-patterned CD SAMs in PMMA structures were immersed into a solution of dendrimer (0.01 mM in adamantyl functionalities) for 10 min, followed by rinsing with 1 mM CD at pH = 2. The films were then immersed in a solution of CD Au NPs (5.8 μM in cyclodextrin functionalities) for 10 min, followed by rinsing with water. A multilayer structure was formed by alternating these adsorption steps. For the nTP process, oxidized PDMS stamps were inked by immersion into the dendrimer solution (1 mM in adamantyl functionalities) for 15 min. After removal from the solution, the stamps were immersed in a CD Au NPs solution (5.8 μM in cyclodextrin functionalities) for 10 min, followed by rinsing with water. Further LBL assembly was performed as described above.

AFM. AFM experiments were carried out with a NanoScope IIIa Multimode AFM (Digital Instruments, Veeco Metrology Group, USA) in contact mode using V-shaped Si_3N_4 cantilevers (Nanoprobes, Veeco) with a nominal spring constant of 0.12 N/m. The AFM was equipped with a J scanner. To ensure maximum sensitivity for lateral force images, the sample was scanned in 90° with respect to the long axis of the cantiliver. Images were captured in ambient atmosphere (ca. 40−50% relative humidity, 25 °C) unless mentioned otherwise.

Chart 1. Chemical Structures of the Host Adsorbates, the CD Au NPs, and the Adamantyl-Terminated PPI Dendrimers Used in This Study



Results and Discussion

Multilayer thin films composed of CD-modified gold nanoparticles (CD Au NPs) and adamantyl-terminated dendrimers (generation 5 with 64 adamantyl end groups, see Chart 1)[25] have been patterned on CD SAMs using several lithographic techniques such as μCP[36] and NIL.[37] CD SAMs were prepared both on gold[19] and on silicon oxide[20] surfaces. These layers display the same binding properties toward multivalent guest molecules.[20,22,38,39] CD Au NPs were synthesized according to a literature procedure[31] by the reduction of $AuCl_4^-$ in DMSO containing perthiolated β-CD;[27] TEM showed a mean particle size of 2.8 ± 0.6 nm.[32] Adamantyl-terminated PPI dendrimers were synthesized as previously described[29] and were brought into aqueous solution (pH = 2) by the complexation of the adamantyl

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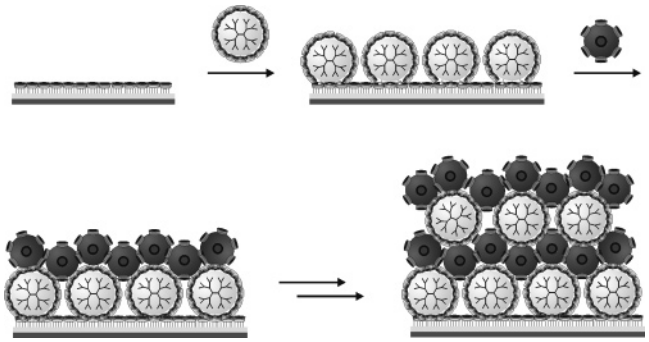
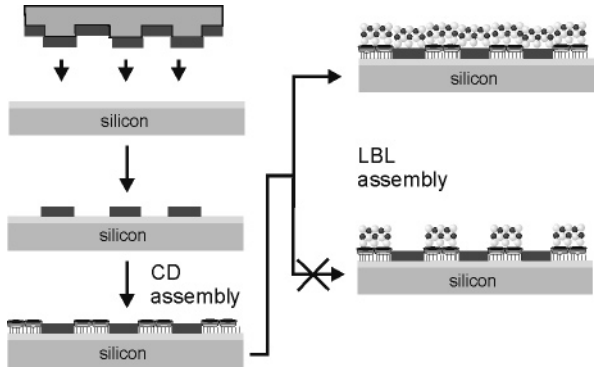
Scheme 1. LBL Assembly Scheme for Alternating Adsorption of Adamantyl-Terminated PPI Dendrimer and CD Au NPs onto CD SAMs



Scheme 2. Preparation of Patterned LBL Assemblies on Chemically Patterned SAMs by Microcontact Printing of an Inert SAM Followed by CD Assembly and LBL Assembly



end groups using a slight excess of cyclodextrin and by the protonation of the dendrimer core amino functionalities.[40] The LBL assembly, the alternating adsorption of the adamantyl-terminated dendrimers and the CD Au NPs, was performed as described before (Scheme 1).[25]

LBL Assembly on μCP- and NIL-Patterned SAMs. Our first approach for patterning supramolecular LBL assemblies utilized the concept of selective deposition on chemically patterned surfaces as a template for multilayer deposition that was introduced by Hammond's group.[11] A schematic representation of the method is shown in Schemes 2 and 3. The goal is to create patterned SAMs, of which one type of area consists of CD SAMs suitable for LBL assembly, while the remaining areas resist adsorption of both LBL components. We have used μCP- and NIL-patterned CD SAMs to achieve selective LBL deposition, with various adsorption-resisting SAMs in between to prevent nonspecific LBL assembly in these areas. μCP-patterned CD SAMs on gold (Scheme 2) were prepared by μCP of mercapto-oligo-(ethyleneglycol) (EG)[30] or 11-mercaptoundecanol (OH), followed by CD SAM formation from solution in the other (bare) regions.[19] NIL-patterned CD SAMs (Scheme 3) were obtained by metal evaporation of a layer of 20 nm gold on PMMA-imprinted silicon oxide substrates followed by metal liftoff.[34] Various inert silanes (amino-terminated, PEG-terminated, or none) were deposited from the gas phase onto the bare silicon oxide areas. CD heptathioether assembly was

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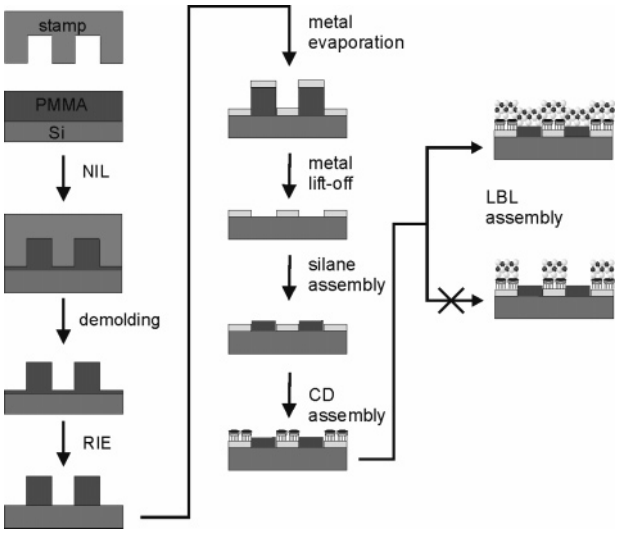
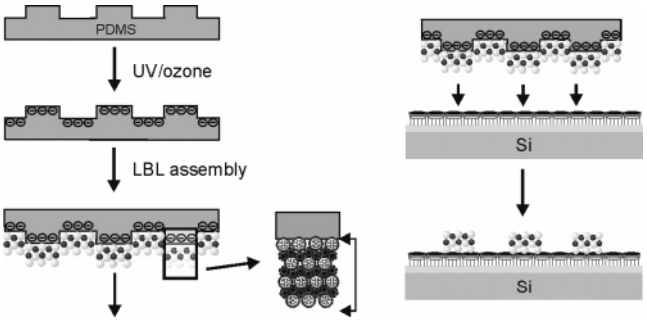
Scheme 3. Preparation of Patterned LBL Assemblies on Chemically Patterned SAMs by Nanoimprint Lithography (Left); Metal Evaporation and Liftoff, Formation of an Inert Silane SAM, and CD Assembly (Center); LBL Assembly (Right)



Scheme 4. Preparation of Patterned LBL Assemblies by Nanotransfer Printing, Which Consists of Oxidation of the PDMS Surface, LBL Assembly on the PDMS Stamp, and Contacting It with a CD SAM



performed on the NIL-patterned gold regions as described before.[19]

Patterned SAMs created by μCP or NIL were alternately immersed into solutions of the adamantyl-terminated dendrimer and of CD Au NPs (0.01 mM for the dendrimer and 5.8 μM for the CD Au NPs, in supramolecular functionalities), after each adsorption step rinsed with a concentrated CD solution and water. AFM was used to characterize the chemically patterned surfaces before and after the LBL assembly. AFM images (data not shown) indicated that the LBL assembly was nonspecific, i.e., not only on the CD regions but also on the (intentionally resistant) silane regions. The lack of specificity for the LBL assembly is attributed to strong hydrophobic interactions caused by the dendrimer deposition and to the relatively low solubility of these dendrimers. These results led us to investigate different methodologies for patterning these hybrid supramolecular LBL assemblies.

Nanotransfer Printing of LBL Assemblies. A schematic representation of the nanotransfer printing (nTP)[15,16] method is shown in Scheme 4. PDMS stamps with 10 μm lines and dots were oxidized by a UV/ozone (UVO) treatment, resulting in a negatively charged surface.[41] Subsequently, the

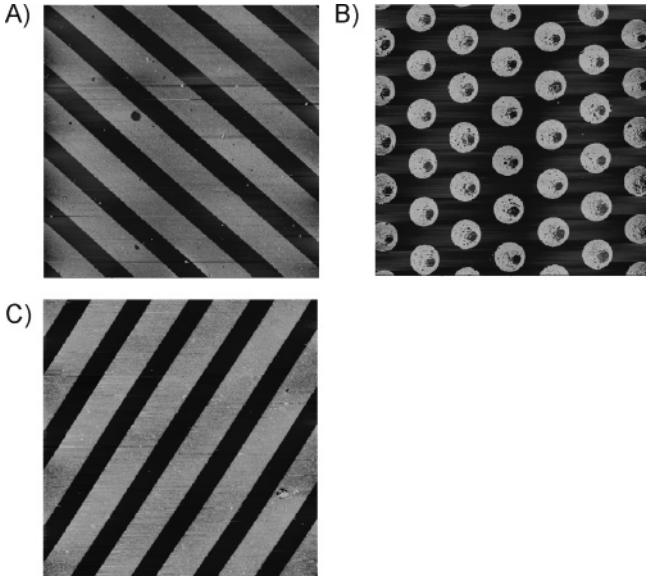


Figure 1. Contact mode AFM height images (80 × 80 μm^2, *z* range 30 nm) of lines of two bilayers (A), dots of four bilayers (B) of dendrimer/CD Au NPs, each with an additional dendrimer layer on top (see Scheme 3), after nanotransfer printing onto a CD SAM, and four bilayers (C) of dendrimer/CD Au NPs after nanotransfer printing with a CD Au NPs-terminated PDMS stamp to a dendrimer-covered CD SAM.

slightly negatively charged stamps were immersed in an aqueous solution of the dendrimer (1 mM in adamantyl functionalities) to allow adsorption of one layer of dendrimers onto the stamp based on electrostatic interactions. Hereafter, alternating adsorptions of CD Au NPs and dendrimer (5.8 μM in cyclodextrin functionalities and 0.01 mM in adamantyl functionalities, respectively) with rinsing steps in between yielded a complete multilayer on the stamp surface, both on the protruding and recessed stamp areas. As the last layer, a dendrimer layer was deposited, thus promoting host−guest interactions between the multilayer stack on the stamp and the CD SAM on the substrate. The patterned PDMS stamp with the multilayer thin film was put into contact with the CD substrate for 5 min. After removal of the stamp, the substrate was thoroughly rinsed with aqueous 1 mM CD (pH = 2) and water and dried under a flow of N_2.

Transfer of the multilayer stacks was visualized by atomic force microscopy (AFM) imaging as shown in Figure 1.[42] Unless noted otherwise, the stacks were transferred completely; i.e., no material remained on the protruding PDMS stamps after contact. Apparently, the electrostatic interactions between the PDMS stamp and the first dendrimer layer, arising from the slightly negative charge of the silica-like oxidized PDMS top layer and the positively charged dendrimer cores, are weaker than the host−guest interactions between the last dendrimer layer and the CD SAM. The transferred multilayer thickness as a function of the number of deposited bilayers is shown in Figure 2, indicating a linear thickness increase of approximately 3 nm per bilayer. This is somewhat higher than the thickness increase observed on unpatterned substrates (2 nm per bilayer).[25] Nevertheless, it

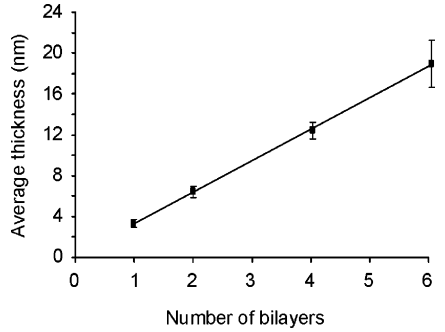


Figure 2. Multilayer thickness after nTP as a function of the number of bilayers assembled onto the CD SAM as measured by AFM.

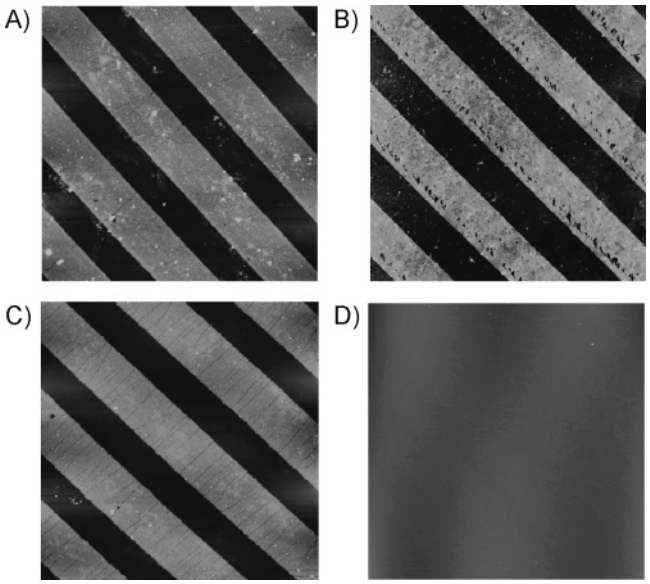


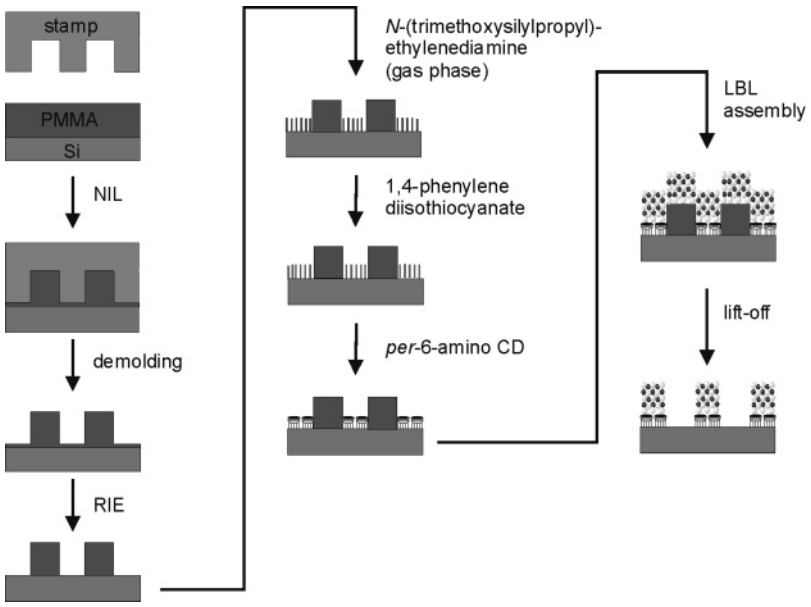
Figure 3. Contact mode AFM height images (50 × 50 μm^2, *z* range 60 nm for A, B, and *z* range 40 nm for C, D) before (A, C) and after (B, D) rinsing (with 1 mM CD and water) of CD SAM substrates with four bilayers (A, C) and six bilayers (B, D) nanotransfer-printed LBL assemblies, using a dendrimer-terminated stamp on a dendrimer-covered CD SAM (A, B) or a CD Au NPs-terminated stamp on a (empty) CD SAM (C, D).

can be concluded that the nTP of the complete multilayer stacks is accomplished successfully. In a similar manner, the nTP can also be accomplished faithfully (Figure 1C) when a LBL assembly ending in CD Au NPs on the stamp is contacted with a dendrimer-covered CD SAM (adsorbed from solution using a 0.01 mM solution in adamantyl functionalities).

The supramolecular specificity of the multilayer transfer was tested by two control experiments. In the first, a dendrimer layer (0.01 mM in adamantyl functionalities) was adsorbed on the CD SAM prior to nTP. The dendrimer-covered CD SAM substrate was thoroughly rinsed with 1 mM CD and water before the multilayer transfer. LBL assembly was performed onto the PDMS stamp as described above, ending in a dendrimer layer as well. Subsequently, the stamp was placed on the dendrimer-covered CD SAM applying contact for 5 min. Transfer of the LBL assembly was observed, as illustrated by AFM (Figure 3A). Transfer of four bilayers showed a thickness of 16 nm, comparable to the results given above. After thorough rinsing with 1 mM CD and water, the multilayer structures remained (Figure 3B). Apparently, nonspecific, hydrophobic interactions are in this case strong enough to retain the LBL assemblies on

(41) Efimenko, K.; Wallace, W. E.; Genzer, G. *J. Colloid Interface Sci.* **2002**, *254*, 306−315.
(42) Note that the "holes" present on the dot structures are due to a stamp artifact.

Scheme 5. Preparation of NIL-Patterned LBL Assemblies Using NIL (Left), CD Monolayer Formation (Center), and LBL Assembly and Liftoff (Right)



the substrate. In a second control experiment, a layer of CD Au NPs was deposited at the end of the multilayer stack on the stamp, which was put into contact with a (empty) CD SAM. AFM showed that the multilayer stack was transferred (Figure 3C). However, after the substrate was rinsed extensively with aqueous 1 mM CD followed by water, the multilayer pattern was removed completely from the CD substrate, indicating, in this case, the need for specific supramolecular interactions for maintaining stable LBL assemblies on the substrates (Figure 3D).

LBL Assembly on NIL-Patterned PMMA Templates. To pattern multilayer thin films, a third multistep process was developed, which involves the combination of NIL and LBL assembly.[35] Possible advantages of the integration with NIL are as follows: (i) high resolution of NIL[35,37] and (ii) possibility to remove nonspecifically adsorbed material by liftoff from the PMMA substrates. The integrated scheme of the two multistep processes is shown in Scheme 5. The left part shows the NIL process, resulting in patterned PMMA structures with native silicon oxide areas in between. The center part shows the process to create the CD SAMs on the silicon oxide areas, employing the PMMA structures as a physical barrier for the CD pattern.[20,35] The right part shows the LBL assembly on the NIL-patterned substrates and the polymer removal, resulting in patterned LBL structures.

Patterned substrates containing various micrometer structures were prepared using spin-coated PMMA layers of 400 nm thickness, followed by NIL ($T = 180$ °C, $p = 40$ bar). The residual PMMA layer was removed by acetone treatment.[34] The silicon oxide areas in between were further functionalized in a three-step process, resulting in patterned CD monolayers on silicon oxide using a methodology previously described.[20,35] AFM confirmed the expected layer thickness of 2.8 nm for a CD-patterned sample which was subjected to acetone and ultrasound prior to AFM imaging in order to remove the PMMA.[35] These results were similar to the ones obtained for a full CD SAM.[20] LBL assembly was performed on the NIL-patterned substrates as described above. Since the LBL assembly was performed in aqueous solution, damaging or dissolution of the PMMA structures does not occur. Multilayer deposition took place in the CD regions as well as on the PMMA. Hereafter, the PMMA structures, with the nonspecifically adsorbed LBL material, were removed in acetone using ultrasonication.

Figure 4 shows various NIL-patterned LBL structures with different numbers of bilayers. A thickness increase per bilayer of only about 1.1 nm was observed (Figure 5). LBL assembly on full substrates, subjected to the same liftoff procedure, yielded comparable thicknesses (as witnessed by AFM scratching experiments) before and after the treatment. Also, acetone treatment on nTP-patterned substrates did not result in a decrease of feature height of these LBL assemblies. Thus, it was concluded that the lower thickness values for

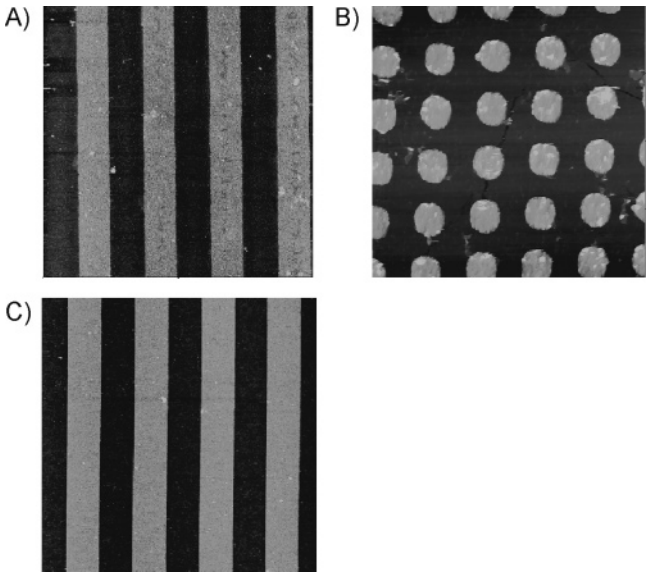


Figure 4. Contact mode AFM height images of LBL assemblies on NIL-patterned PMMA-CD SAM structures after PMMA removal. AFM images show micrometer lines and dots of 4 bilayers (A; 40 × 40 μm^2, z range 30 nm), 10 bilayers (B; 10 × 10 μm^2, z range 40 nm), and 20 bilayers (C; 40 × 40 μm^2, z range 60 nm).

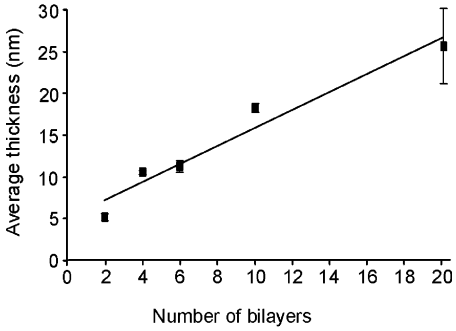


Figure 5. Multilayer thickness after NIL patterning, LBL, and liftoff (Scheme 4) as a function of the number of bilayers assembled onto the CD SAM as measured by AFM.

NIL patterning, compared to LBL assembly on full layers and nTP assemblies, do not result from the liftoff procedure, but possibly from different wetting and mass transport limitations of the LBL components on the PMMA-structured substrates. Nevertheless, the linear growth observed in this case as well (Figure 5) shows the potential of NIL for structuring LBL assemblies.

Conclusions

Various patterning strategies have been applied to create 3D structures of supramolecular LBL assemblies on CD molecular printboards. Microcontact printing and NIL followed by metal evaporation and liftoff have been performed in order to obtain chemically patterned SAMs to attempt directed LBL assembly, relying on the chemical specificity. These two approaches did not lead to patterned LBL assemblies. The observed indiscriminate LBL adsorption was attributed to nonspecific adsorption of the dendrimer. In contrast, patterned LBL assemblies were obtained faithfully by nTP. They showed good stability against rinsing, even with a monovalent competitive host in solution, and against acetone/ultrasound treatment. Supramolecular specificity was observed, but was not perfect, again due to nonspecific interactions induced by the dendrimer. Dendrimers with a higher solubility[43] may suppress these nonspecific interactions. Patterned LBL assemblies by nanoimprint lithography, LBL assembly, and liftoff have been obtained using PMMA as a physical barrier for the multilayer deposition. Differences in the multilayer heights as a function of the number of bilayers have been observed for the various methods, which are partly explained by wetting differences.

With the combining of top-down and bottom-up approaches, hybrid organic/metal NPs nanostructures have been obtained with control over all three dimensions, *x*, *y* by the top-down methods and *z* by the LBL assembly. These methodologies can in principle be used in other nanofabrication schemes and may lead to well-defined, high-resolution 3D nanostructures of a large variety of materials.

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(43) Nijhuis, C. A.; Yu, F.; Knoll, W.; Huskens, J.; Reinhoudt, D. N. *Langmuir* **2005**, *21*, 7866−7876.