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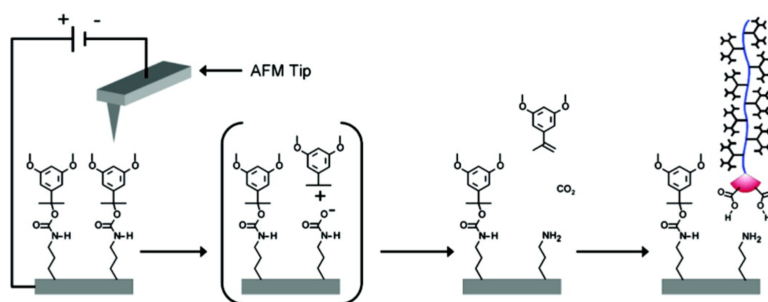

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AFM-Induced Amine Deprotection: Triggering Localized Bond Cleavage by Application of Tip/Substrate Voltage Bias for the Surface Self-Assembly of Nanosized Dendritic Objects

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Surface modification has been extensively studied because of its great utility in applications ranging from lithography[1] to bioanalysis.[2] Surface functionalization with an amine monolayer is especially popular because of the high reactivity of amine surfaces toward both covalent attachment[3] and ionic self-assembly.[4] Patternwise fabrication of amine monolayers has been previously accomplished on the micrometer scale using light,[5] and on the nanometer scale using classical e-beam lithography[6−12] or AFM.[13] We wish to report the localized chemical activation of a protected amine surface by the application of a voltage bias between the tip of an atomic force microscope (AFM) and a silicon substrate. The latent amine patterns are visualized by the self-assembly of dendritic carboxylates.

The α,α-dimethyl-3,5-dimethoxybenzyloxycarbonyl (DDZ) group has been used as a photocleavable amine-protecting group in peptide synthesis,[14,15] as well as a photobase generator in lithography.[16] The commonly accepted mechanism for photochemical deprotection is heterolytic bond cleavage followed by elimination of the carbocation to release 3,5-dimethoxy-α-methylstyrene, carbon dioxide, and a primary amine.[16] The structure of our monolayer precursor **1**[17] and mechanism of photochemical cleavage is shown in Figure 1.

The fact that cleavage of the DDZ group proceeds via ionic, rather than radical, intermediates was a determining factor in our choice of this group. We postulated that the intense local electric field that can be produced by an AFM tip would exert a force on an already polarized bond. Therefore, an ionic reaction would be more likely to be triggered by this stimulus than a reaction that proceeds via radical intermediates, such as the photochemical deprotection of 2-nitrobenzylcarbamates. Furthermore, in contrast to 2-nitrobenzylcarbamates, which produce both carbonyl and nitroso groups, the only byproducts of DDZ cleavage are 3,5-dimethoxy-α-methylstyrene and carbon dioxide.[15] While both carbonyl and nitroso compounds are prone to recombination with amines, 3,5-dimethoxy-α-methylstyrene is not reactive.

The protected amine monolayer was prepared by immersing a freshly cleaned and hydroxylated silicon wafer in a solution of **1** in dry toluene. The monolayer was pattered using an AFM operating in tapping mode with a conducting tip. Typically, the amplitude set point was reduced to ca. 10% of the imaging amplitude, and the tip was translated across the surface (1−10 μm/s) while applying a +12 V potential to the sample and grounding the tip. To avoid local anodic oxidation of the underlying substrate,[18] all of the patterning was performed under an inert atmosphere. After pat-

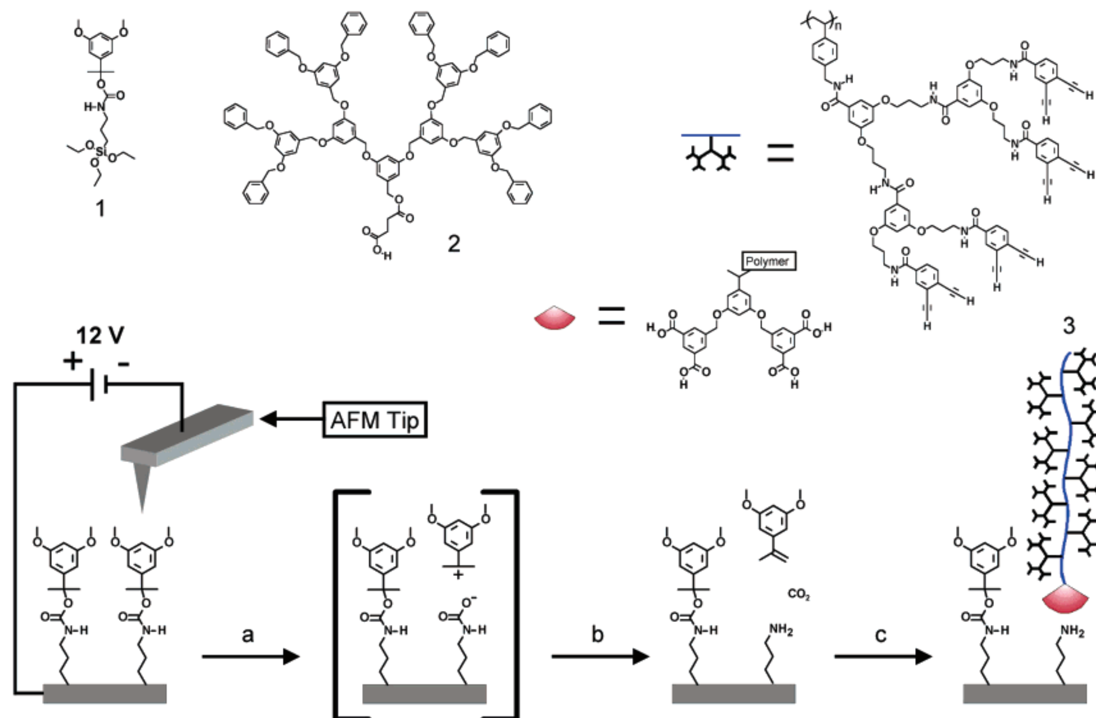

Figure 1. Structure of monolayer precursor (1), dendron (2), dendronized polymer (3), and schematic of surface deposition procedure. (a) Heterolytic bond cleavage. (b) Release of carbon dioxide and 3,5-dimethoxy-α-methylsytrene to reveal primary amine. (c) Ionic self-assembly of dendritic macromolecules forming a relief pattern.

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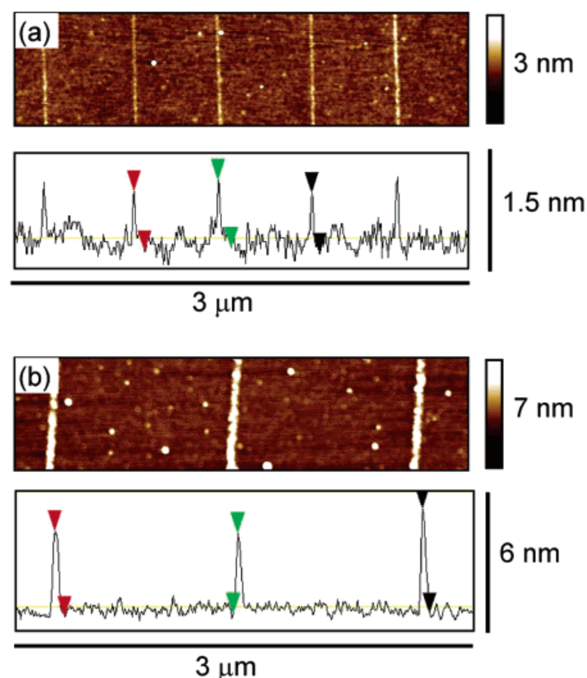

Figure 2. AFM images and height profiles. (a) Lines made from dendrimer (**2**) are 25 nm wide and 1 nm tall. (b) Lines made from dendronized polymer (**3**) are 35 nm wide and 4 nm tall.

terning, the substrate was placed in a solution of the appropriate dendritic macromolecule for 24 h, rinsed thoroughly, and returned to the AFM for imaging (tapping mode). The width of the amine lines is affected by the amplitude set point, scan rate, and applied voltage bias. AFM images of lines formed from dendrimer **2** and dendronized polymer **3** are shown in Figure 2, parts a and b, respectively. The larger molecule produces wider features because of the flexibility of the chain as well as tip convolution effects. An advantage of this process is that the deprotection and assembly sequence does not affect the carbamate in the unexposed regions. Therefore, it should be possible to repeat the process and deposit several distinct materials onto a surface with nanometer scale resolution.

Dendritic macromolecules are ideal candidates for visualization of the latent amine features because they add significant steric bulk while their compact structure minimizes line broadening. In this study, two dendritic molecules with dramatically different dimensions were deposited onto the patterned amine regions of the surface. A G3 benzyl ether dendron with a carboxylic acid at the focal point, **2**, produced lines ca. 1 nm in height (Figure 2a). The theoretical radius for this dendrimer in its fully extended conformation is 2 nm. To create more robust features, we also prepared dendronized linear polymer **3** with a tetradentate carboxylic acid binding group at one chain end. A multidentate binding group was thought to be necessary to anchor such a large molecule (M_n = ca. 60 kDa) onto the surface. The main chain of polymer **3** has a polydispersity index (PDI) of 1.06, which translates directly into low length dispersity of the final "nano-objects." The periphery of the dendronized polymer **3** contains aromatic *ortho*-diynes, which are well-known to cyclize via the Bergman cyclization to generate a new aromatic ring and a diradical.[19] Under concentrated conditions, this diradical species can condense, producing highly robust cross-linked material.[20] DSC shows that this polymer undergoes complete and irreversible cross-linking at 140 °C. Deposition of polymer **3** produced lines approximately 4 nm in height (Figure 2b). The theoretical length of this polymer (all-trans conformation) is 10 nm. The production of 4 nm relief features from a patterned monolayer constitutes a form of "physical amplification", distinct from the chemical amplification process well-known in conventional lithography.[21]

In summary, we have achieved patternwise fabrication of a primary aliphatic amine surface on the nanometer scale and shown that the amines are active toward ionic self-assembly. The relationship between the size of the macromolecule and the height of the resulting features is strong evidence that the features are indeed composed of these molecules. We expect that this process will be applicable wherever amines can be used to selectively assemble materials onto a surface. Specifically, the use of amines for deposition of resist materials for lithography, electroless metalization, device assembly, and protein binding can all be applied on the nanometer length scale. This work potentially provides a method for sequential patternwise deposition of single molecules and may be applied to the surface assembly of more complex molecular machines.

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Supporting Information Available: Experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) McCoy, K.; Gumieny, C.; Hess, D. W.; Tolbert, L. M.; Henderson, C. L. *Proc. SPIE-Int. Soc. Opt. Eng.* **2002**, *4690*, 1025−1033.
(2) Osruni, E.; Yan, L.; Whitesides, G. M. *Colloids Surf., B* **1999**, *15*, 3−30.
(3) Strother, T.; Hamers, R. J.; Smith, L. M. *Nucleic Acids Res.* **2000**, *28*, 3535−3541.
(4) Tully, D. C.; Trimble, A. R.; Fréchet, J. M. J. *Chem. Mater.* **1999**, *11*, 2892−2898.
(5) Brockman, J. M.; Frutos, A. G.; Corn, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 8044−8051.
(6) Gölzhäuser, A.; Eck, W.; Geyer, W.; Stadler, V.; Weimann, T.; Hinze, P.; Grunze, M. *Adv. Mater.* **2001**, *13*, 806−809.
(7) Eck, W.; Stadler, V.; Geyer, W.; Zharnikov, M.; Gölzhäuser, A.; Grunze, M. *Adv. Mater.* **2000**, *12*, 805−808.
(8) Geyer, W.; Stadler, V.; Eck, W.; Gölzhäuser, A.; Grunze, M.; Sauer, M.; Weimann, T.; Hinze, P. *J. Vac. Sci. Technol., B* **2001**, *19*, 2732−2735.
(9) Schmelmer, U.; Jordan, R.; Geyer, W.; Eck, W.; Gölzhäuser, A.; Grunze, M.; Ulman, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 559−563.
(10) Gölzhäuser, A.; Geyer, W.; Stadler, V.; Eck, W.; Grunze, M.; Edinger, K.; Weimann, T.; Hinze, P. *J. Vac. Sci. Technol., B* **2000**, *18*, 3414−3418.
(11) Zharnikov, M.; Grunze, M. *J. Vac. Sci. Technol., B* **2002**, *20*, 1793−1807.
(12) Kim, C. K.; Jung, J. W.; Kim, M.; Kang, T.; Ihm, K.; Kim, K.; Kim, B.; Park, J. W.; Nam, H.; Hwang, K. *Langmuir* **2003**, *19*, 4504−4508.
(13) Liu, S.; Maoz, R.; Sagiv, J. *Nano Lett.* **2004**, *4*, 845−851.
(14) Birr, C.; Lochinger, G.; Stahnke, G.; Lang, P. *Liebigs Ann. Chem.* **1972**, *763*, 162−172.
(15) Pillai, V. N. R. *Synthesis* **1980**, 1−26.
(16) Cameron, J. F.; Fréchet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5919−5922.
(17) Jennane, J.; Boutros, T.; Giasson, R. *Can. J. Chem.* **1996**, *74*, 2509−2517.
(18) Ma, Y. R.; Yu, C.; Yao, Y. D.; Liou, Y.; Lee, S. F. *Phys. Rev. B* **2001**, *64*, 195324-1−195324-5.
(19) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660−661.
(20) Chen, X.; Tolbert, L. M.; Hess, D. W.; Henderson, C. L. *Macromolecules* **2001**, *34*, 4104−4108.
(21) MacDonald, S. A.; Willson, C. G.; Fréchet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151−158.

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