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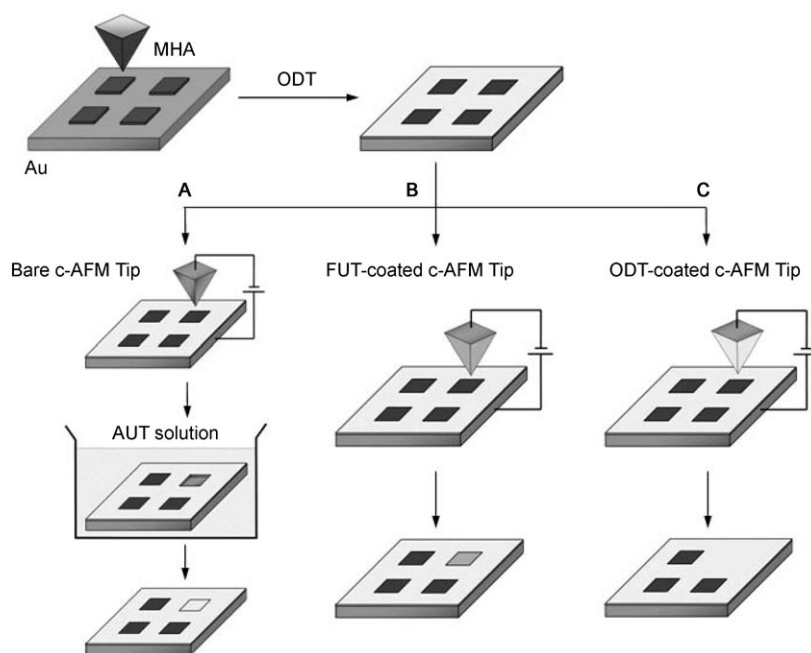
A “Molecular Eraser” for Dip-Pen Nanolithography**

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Dip-pen nanolithography (DPN)^[1,2] has evolved into a powerful nanolithographic tool for generating molecule-based structures on a wide variety of surfaces. The technique and variants of it have been used to create metal and semiconductor nanostructures,^[3–5] biological arrays (including proteins,^[6] DNAs,^[7] viruses,^[8] bacteria,^[9] and cells^[6]), carbon-nanotube^[10] affinity templates, and arrays of magnetic nanoparticles,^[11,12] Au nanoparticles,^[13,14] and conducting polymers.^[15] In addition, DPN recently has been transformed from a serial to a massively parallel process through the use of both one- and two-dimensional cantilever arrays.^[16,17] As more applications are identified for the technique, the demand for additional capabilities increases. Thus far, no one has explored the development of repair approaches for the structures generated in a DPN experi-

ment. As with macroscopic writing techniques, an erasing method would allow the elimination or repair of defective nanostructures, and modify existing ones in order to create more sophisticated architectures and materials.

There are at least two potential routes to developing a molecule-based eraser for DPN-generated structures. One involves the physical removal of a portion of a monolayer structure, akin to nanografting,^[18–20] but in the context of a preformed nanostructure. The second involves the use of a



Scheme 1. Schematic illustration of the steps associated with the selective desorption of MHA features and in situ replacement with new alkanethiol molecules. Initially, an array of MHA features is generated by DPN, and the surrounding regions are passivated with ODT. A) A selected MHA nanostructure is selectively eliminated by bias scanning a square region that includes this feature with a bare tip. The resulting bare gold area can then be filled with another molecule (e.g., AUT) by dipping this substrate in a solution of a desired alkanethiol. B) Selective elimination and in situ replacement of a MHA nanostructure with FUT by bias scanning a square region that includes this feature with a FUT-coated tip. C) “Molecular erasing” of a MHA nanostructure by bias scanning a square region that includes this feature using an ODT-coated tip.

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conducting tip and conductive atomic force microscope (c-AFM) to electrochemically induce desorption^[21–24] in a site-specific manner. We have taken the latter approach, and herein show that one can repair an existing structure by the selective electrochemical removal of portions in a site-specific manner, or removal with subsequent deposition of a second adsorbate (Scheme 1).

This work was inspired by the observation that one can use a reducing potential to selectively remove alkanethiolate monolayers from gold surfaces where the reduction potential required depends upon the type of adsorbate.^[25,26] In addition, c-AFM has been used in lithographic experiments involving Si substrates where the substrate can be selectively oxidized in the regions scanned.^[27–30] We hypothesized that c-AFM could be used to selectively desorb portions of a monolayer-based structure made by DPN with alkanethiol

inks on gold. To test this hypothesis, we initially used c-AFM to study the behavior of bulk 16-mercaptohexadecanoic acid (MHA) and 1-octadecanethiol (ODT) self-assembled monolayers (SAMs) on Au surfaces as a function of the negative bias voltage applied between the tip and surface. Both SAMs were prepared according to literature procedures^[31–34] by exposing a Au substrate to an ethanolic solution of the desired alkanethiol (1 mM) for one hour, followed by copious rinsing with ethanol and drying with N₂. A series of eight 2- μ m-long lines with widths that vary as function of bias voltage (range = –1 to –15 V in –2 V increments) were then written on both SAMs at a tip speed of 0.05 μ m s^{–1} under ambient conditions ($\approx$ 35% relative humidity, 23 °C). Figure 1 shows contact-mode AFM (CM-AFM) topographic images for both SAMs with the c-AFM written features. For the MHA SAM, lines form at bias voltages more negative than –5 V and exhibit a depth of 1.8 ± 0.3 nm, which is attributed to the reductive desorption of MHA.^[35–39] The ODT SAM exhibits different behavior. Lines begin to form at –7 V but are clearly seen at bias voltages greater than –9 V. Interestingly, protrusions rather than recessed areas are observed, which others have attributed to local oxidation of the silicon underneath the ODT SAM.^[40]

To further evaluate the process involving MHA desorption, we used DPN to prepare a gold substrate with a 3- μ m dot of MHA. The surrounding area was passivated with ODT by immersing the substrate in an ethanolic solution of the alkanethiol (1 mM) for 10 min followed by copious rinsing with ethanol and water. We then used c-AFM to repeatedly scan (three times) a square region within the dot at –5 V. This resulted in the formation of a recessed ($\approx$ 1.8 nm) square feature within the MHA dot (Figure 2). To prove that this feature was the result of MHA elimina-

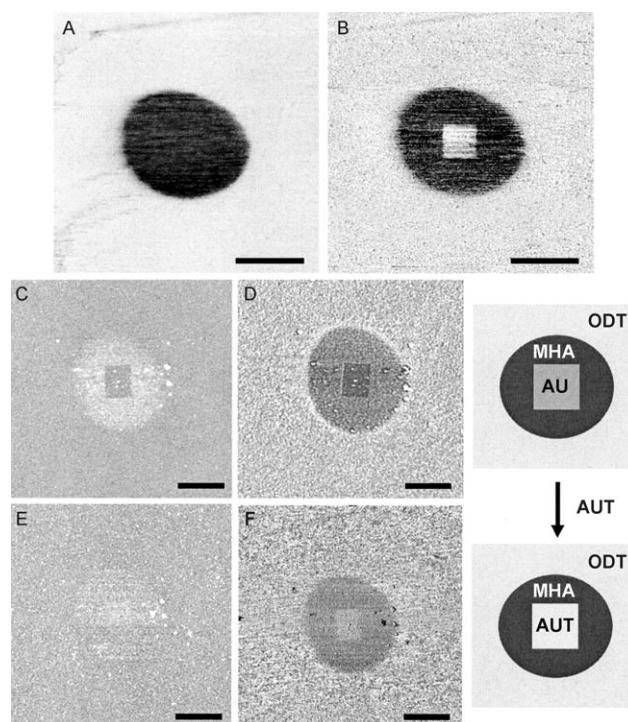


Figure 2. A) Lateral force microscopy (LFM) image of a MHA dot with the surrounding gold regions passivated with ODT. B) LFM image of a square feature generated by eliminating the MHA from the original dot by bias scanning. TM-AFM height (C, E) and phase images (D, F) of the nanostructure shown in (B) before (C, D) and after (E, F) exposure of this substrate to an ethanolic solution of AUT. Scale bars are 1.5 μ m.

tion, the substrate was then exposed to an ethanolic solution of 11-aminoundecanethiol (AUT, 1 mM) for 10 min. After

rinsing the substrate with ethanol to remove any non-specific binding, tapping-mode AFM (TM-AFM) topographic images show that the square feature and the MHA dot feature are close to the same height (compare Figure 2C and E). Furthermore, the phase images before and after exposure of the substrate to the AUT solution show an inversion in contrast between the square feature (from black to white) and the surrounding MHA SAM (Figure 2D and F). Both observations are consistent with the filling of the square nanostructure with AUT and, therefore, with the desorption of the MHA SAM in the square region scanned at –5 V. Interestingly, the formation of

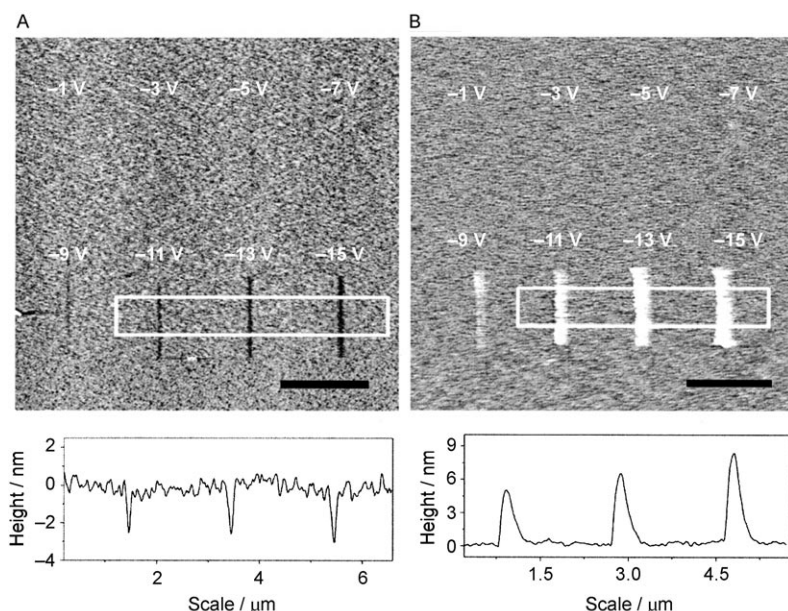


Figure 1. A, B) Contact-mode AFM topographic images and height profiles of c-AFM-written 2- μ m-long lines at bias voltages in the range of –1 to –15 V on MHA (A) and ODT (B) SAMs. Corresponding plots show analysis of highlighted regions in each topographic image. Scale bars are 2 μ m.

this nanostructure points toward the possibility of using this technique to create more complex multiple-ink nanostructures.

By controlling the applied bias in the range of -5 to -9 V, one can use c-AFM to selectively control the elimination of MHA-nanostructures at specific substrate areas in the presence of other features made of MHA and in a sea of passivating ODT. For example, an array (2×2) of 500-nm MHA dots was generated by DPN with the surrounding area passivated with ODT, as described above (Figure 3 A). Square regions ($1 \mu\text{m}^2$) involving the features we wanted to remove were repeatedly scanned (three times) by c-AFM at -5 V at a scan speed of $0.5 \mu\text{m s}^{-1}$. Using this procedure, we could reproducibly and deliberately remove the MHA dot feature with no detectable damage to the ODT-coated regions of the substrate (Figure 3 A and B, upper-left corners). The effectiveness and reproducibility of this approach were confirmed by removing a second MHA dot (bottom, right) using the same conditions (Figure 3 B and C, lower-right corner).

An exciting possibility is the potential to combine c-AFM-induced desorption with DPN deposition by using a doped Si conducting tip coated with a replacement ink. The Si tip was selected because it is easier to coat with an alkanethiol ink without adsorption, which is not the case

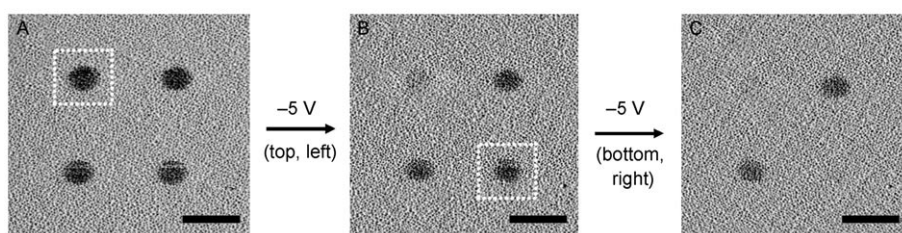


Figure 3. LFM images showing the selective elimination of MHA dots by c-AFM. A) Initial array (2×2) of 500-nm-diameter MHA dots generated by DPN with the surrounding regions passivated with ODT. The dotted square shows the bias-scanned area. B) Selective elimination of the first MHA dot (top, left) by scanning a $1 \mu\text{m}^2$ square area at -5 V. The dotted square shows the bias-scanned area. C) Selective elimination of a second MHA dot (bottom, right) using the same conditions. Scale bars are $1 \mu\text{m}$.

with Au- or Pt/Ir-coated tips. To test the prospect for merging these two techniques, we prepared a gold substrate with a bulk SAM of MHA. When the conductive tip coated with ODT was scanned across a $1 \mu\text{m}^2$ region of the SAM-coated substrate at a bias voltage of -5 V (tip speed of $0.5 \mu\text{m s}^{-1}$), the MHA was removed and backfilled with ODT (Figure 4). Unlike the situation that involved desorption without backfilling, in this case no height difference can be observed in both topographic images (Figure 4 A and C). However, lateral force microscopy (LFM) images show a bright (low-friction) square in the scanned region, which is consistent with the conclusion that the MHA has been replaced with ODT (Figure 4 B and D).

In the previous experiment, little chemical information about the resulting structures is provided. To obtain more chemical information about the structures that form and to demonstrate greater generality, we moved to a three-ink

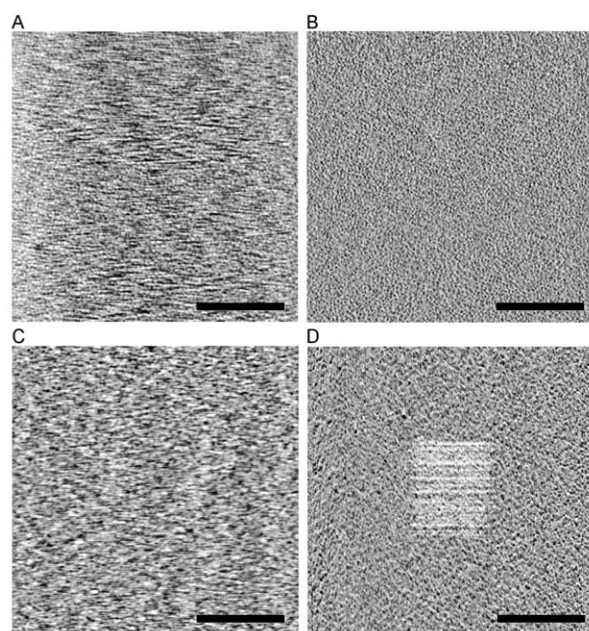


Figure 4. CM-AFM topographic and LFM images of a MHA SAM before (A, B) and after (C, D) bias scanning a $1 \mu\text{m}^2$ square region at -5 V with an ODT-coated tip. Scale bars are $1 \mu\text{m}$. The height scale and surface roughness in (A, C) are 5 nm and ≈ 0.3 nm, respectively.

system. In this experiment, we prepared a 2×2 array of MHA triangles by DPN, and the regions surrounding these features were passivated with ODT (Figure 5 A). A $1 \mu\text{m}^2$ square region that includes a preselected MHA triangle (top, right) was scanned at -5 V (tip speed of $0.5 \mu\text{m s}^{-1}$, under ambient conditions) with a doped Si tip coated with 11-ferrocenyl-1-undecanethiol (FUT, Figure S1 in the Supporting Information).

This procedure results in the elimination of the MHA-based triangle and replacement with a FUT-based one. Since the length of the MHA and FUT are similar and the frictional-force profiles of SAMs made of them are nearly identical, AFM and LFM do not provide much information about the chemical content of the resulting triangle (Figure 5 B). However, since the MHA has a reactive carboxylate end and the FUT does not, we were able to use coordination chemistry^[41] to demonstrate post-functionalization of the MHA features in the presence of the FUT triangle; a similar approach was used to study phase separation in ODT and MHA SAMs.^[42] In a typical experiment, the substrate with the 2×2 array of triangles with three MHA features and one post-formed FUT feature was immersed in a 1 mM ethanolic solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ for 15 min, followed by rinsing with ethanol, and further immersion of the sample in a 1 mM ethanolic solution of MHA for 15 min. This process

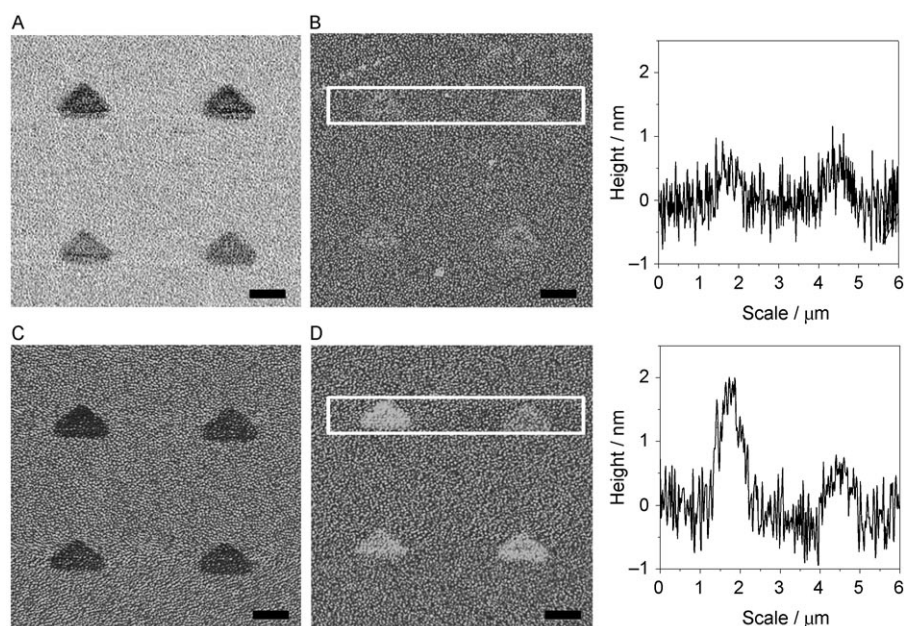


Figure 5. Removal of a MHA-SAM nanostructure and concomitant filling with a FUT-SAM by c-AFM and DPN, respectively. A) LFM image of a 2×2 MHA triangle array with the surrounding region passivated with ODT. B) TM-AFM height image of this array, in which a selected dot (top, right) was scanned at -5 V with a FUT-coated tip. C) TM-AFM phase image and D) corresponding height image of this array after coordinating a layer of Cu^{2+} ions and MHA to the nanotriangle features. The triangle (top, right) scanned at -5 V with a FUT-coated tip does not show a significant height increase while the MHA triangles that were not exposed to the tip have increased in height by 1.8 ± 0.4 nm, consistent with Cu–MHA coordination. Corresponding plots show the average line scans of the highlighted regions. Scale bars are 500 nm.

results in the formation of a second coordinated layer of MHA on the original MHA features on the patterned substrate. After rinsing the sample with ethanol, TM-AFM showed that only the triangular features made of MHA and not the assigned FUT feature increased in height (Figure 5D, compare top right and left triangles). Taken together, these data are consistent with the conclusion that one can selectively replace preformed features with other inks coated on the c-AFM tip. Interestingly, the initial triangular shape of the MHA nanostructure has been maintained (Figure 5C), even though the region scanned was in the form of a square, which demonstrates the high selectivity of the process and distinguishes the technique from grafting processes^[18–20] where replacement takes place everywhere one scans. The generality of the observation will be dependent on ink combinations.

All of the data presented thus far point to the ability to erase and refill selected areas of MHA SAMs with nanometer precision, a capability that could become important for repairing defective molecule-based features made by DPN or other lithography techniques. To evaluate the prospect of such a capability, we generated structures with intentional defects that could be subsequently removed. For example, a MHA triangle with one defective edge was generated by DPN with the surrounding area passivated with ODT (Figure 6A, left). A square region (denoted by the dotted lines) containing the defect was then repeatedly scanned (six times) at -5 V (tip speed = $0.5 \mu\text{m s}^{-1}$) with a doped Si tip

coated with ODT, the same molecule used to passivate the area around the triangular nanostructure. This resulted in the desorption and replacement of the MHA molecules of the defective region with ODT and, therefore, in the repair of the defective MHA triangle (Figure 6A, right). This is a general capability. Indeed, we demonstrated that even letter features can be easily corrected. For example, we intentionally generated a pattern spelling “DRN” (Figure 6B). The “R” could be converted easily to a “P” using a procedure analogous to the one used for the triangle in Figure 6A.

In conclusion, we have reported a new approach to “molecular erasing” that allows the elimination of portions of SAM-based struc-

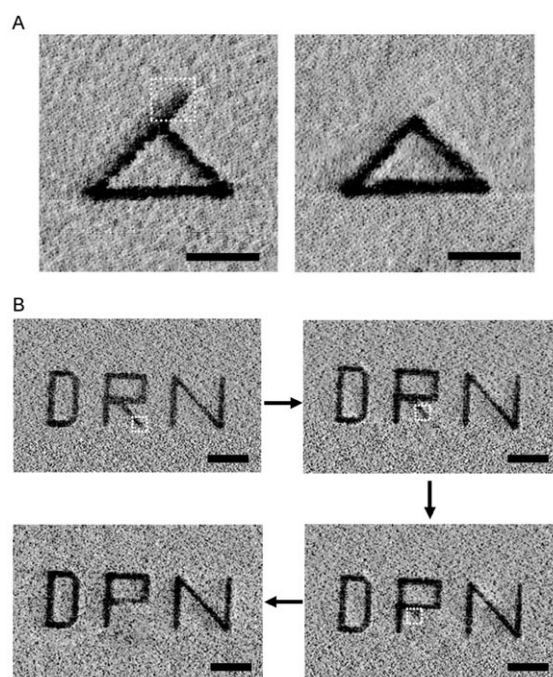


Figure 6. LFM images showing the repair process for a defective MHA polygon and MHA letter by c-AFM and DPN. A) A MHA triangle with a defective top side was repaired to form a perfect triangle by bias scanning at -5 V with an ODT-coated tip. B) The letter “R” was modified to form a “P” by scanning at -5 V with an ODT-coated tip. The scanned area was initially confined to the lower-right portion of the “R” and slowly moved upward and left to remove the line segment (see white dotted boxes, which designate the scanned areas). All the dotted regions were scanned twice. Scale bars are 1 μm .

tures with nanometer precision. In the case of MHA, the dimensions and geometry of the initial nanostructures are well preserved because the surrounding passivating layer is not affected when a bias voltage between -5 V and -9 V is applied. Significantly, this erasing technique can be coupled with DPN, and the eliminated MHA features can then be backfilled in situ with a new ink by simply coating the cantilever with the desired molecule. Since these two techniques can be combined and both methods can be applied to other alkanethiols (Figure S2 in the Supporting Information), researchers can begin to use the tandem techniques not only as repair tools but also for making multifunctional nanostructures not easily generated by normal DPN or other nanolithographic procedures.

Experimental Section

Materials: MHA (90%), ODT (98%), ethanol (200 proof, HPLC grade) and dichloromethane (99.5%) were purchased from Aldrich. FUT ($>95.0\%$) and AUT ($>90.0\%$) were purchased from Dojindo Laboratories. Ti (99.7%), and Au (99.99%) wires were purchased from Alfa Aesar.

Au substrate preparation: Polycrystalline Au films were prepared by thermal evaporation of 7 nm of Ti on SiO_x (Silicon Sense, Inc.) followed by 50 nm of Au at a rate of 0.1 nm s^{-1} and a base pressure below 1×10^{-6} Torr.

Bulk SAM formation: SAMs of alkanethiol molecules were prepared on Au thin films by immersing a substrate in a 1 mM ethanol solution of the corresponding molecules for 1 h, followed by rinsing with ethanol and water, and drying with N_2 .

Conductive-AFM (c-AFM) lithography: The c-AFM was performed with Pt/Ir-coated tips (SCM-PIC, Veeco), sourcemeter (Keithley 2400), and an atomic force microscope (CP, Veeco/Thermomicroscope); dc bias mode was used.

Dip-pen nanolithography (DPN) patterning: DPN-patterning experiments were carried out with an AFM (CP, Veeco/Thermomicroscopes, Sunnyvale, CA) equipped with a 100- μm scanner, closed-loop scan control, and commercial lithography software (DPNWrite, DPN System-1, Nanoink Inc., Chicago, IL). Gold-coated commercial AFM cantilevers (sharpened, Si_3N_4 , Type A, Nanoink Inc.) with a spring constant of 0.05 N m^{-1} were used for patterning and subsequent imaging. All DPN patterning experiments were carried out under ambient conditions ($\approx 30\%$ relative humidity, 23°C). Tips were soaked in a 10 mM acetonitrile solution of MHA or 10 mM dichloromethane solution of FUT, and then blown dry with N_2 . DPN-generated features were prepared on a gold thin film substrate by moving the tip over the surface in the form of the desired pattern.

Combined c-AFM and DPN: Doped Si tips (n^+ Si, resistivity: ~ 0.01 – $0.0025 \Omega\text{cm}$; Nanosensors), which exhibit nearly identical behavior as Pt/Ir-coated tips, were used in order to easily coat the alkanethiols on the tip surface. After coating the tips, these experiments were carried out using the same conditions as the other c-AFM experiments. Thus, a sourcemeter (Keithley 2400) was used for applying a bias voltage, and all experiments were performed with an atomic force microscope (CP, Veeco/Thermomicroscope).

AFM characterization: Contact-mode AFM (CM-AFM) images were taken with a CP AFM system (Veeco Instruments). The images after c-AFM experiments were taken with the same instrument but in normal AFM and LFM mode (no bias voltage). In addition, all LFM images shown are with the tip moving from right to left. Tapping-mode AFM (TM-AFM) images were taken with a NanoMan AFM system (Veeco Instruments).

Supporting Information available: CM-AFM images of a DPN-generated square pattern of 11-ferrocenyl-1-undecanethiol (FUT); CM-AFM images of 16-mercaptophexadecylphosphonic acid and 16-perfluoroundecanethiol-SAMs scanned at different biases. These materials are available free of charge via the Internet at <http://www.small-journal.com>.

Keywords:

alkanethiols • atomic force microscopy • dip-pen nanolithography • self-assembled monolayers

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Supporting Information

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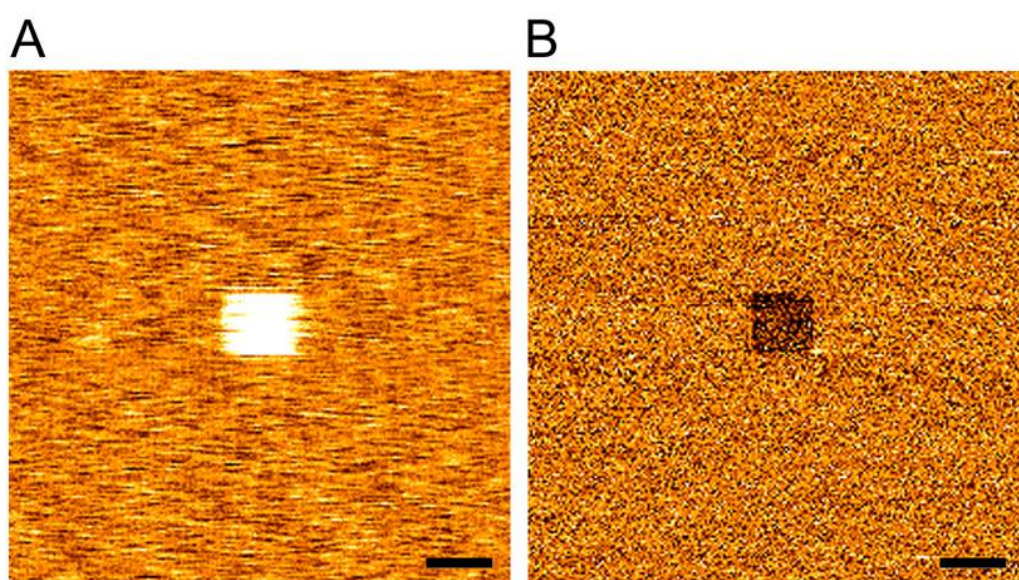


Figure S1. CM-AFM topographic (A) and LFM (B) images of a $1\mu\text{m}^2$ square pattern of FUT generated by DPN. Scale bars are $1\mu\text{m}$.

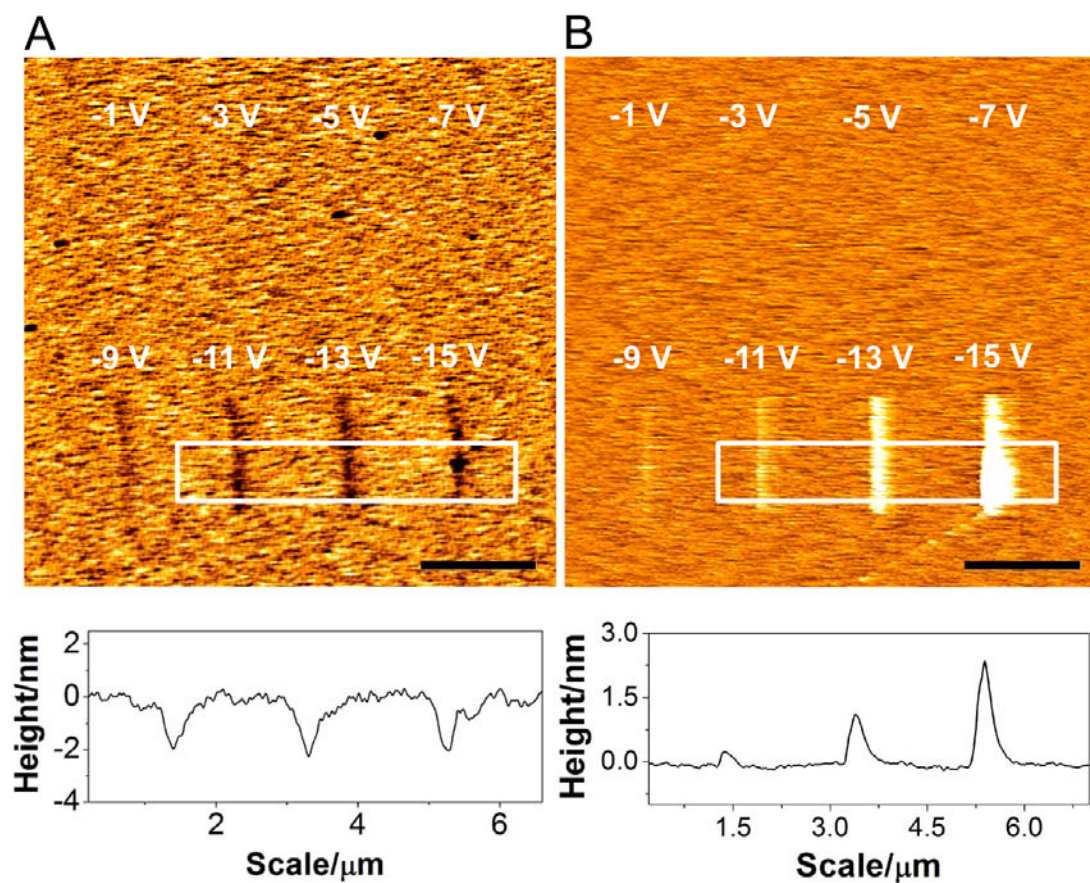


Figure S2. Contact-mode AFM topographic images and height profiles after writing eight 2 μm long lines at bias voltages in the range of -1 to -15 V on (A) 16-mercaptohexadecylphosphonic acid and (B) 16-perfluoroundecanethiol-SAMs. Corresponding plots show analysis of highlighted regions in each topographic image. Scale bars are 2 μm .