Heterogeneous Catalysis of a Copper-Coated Atomic Force Microscopy Tip for Direct-Write Click Chemistry

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Supporting Information

Microcontact Printing of Alkyne Molecules onto Azide-Terminated Silicon Wafer Pieces.

Our procedure for preparing surfaces containing microcontact printed features for comparison to features written via direct-write click chemistry (adapted from Ref. S1) was as follows: Polydimethylsiloxane (PDMS) stamps were prepared from a 10:1 mixture of PDMS-Sylgard Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp. Midland, MI), poured over a fluoro-coated patterned silicon wafer – SAM of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (Gel-est, Inc., Morrisville, PA) – in a Petri dish. The mixture was allowed to stand at room temperature for 1 h before being placed into an oven at 60 °C for 16 h. The cured PDMS was then peeled away from the patterned silicon wafer and cut into ~1 cm² pieces and used as stamps. These stamps were oxidized in UV/ozone plasma (200 W, 10 sec) and stored in deionized H₂O until ready for use. Oxidized PDMS stamps were removed from H₂O and dried under a stream of N₂, and were then immediately inked with 1 drop of 1 mM CuSO₄•5H₂O in EtOH, 1 drop of 2 mM ascorbic acid in EtOH, and 4 drops of 5 mM terminal alkyne in EtOH. This mixture was allowed to combine on the

Figure S1 – 50 × 50 micron region contact mode atomic force microscopy topography (left) and friction (right) images in EtOH of 4-pentynoic acid monolayers stamped onto azide-terminated silicon wafers. Topography image indicates a height of 1.0(2) nm. Friction image indicates the carboxylic acid terminated regions exhibit higher friction than the unreacted (azide-terminated) regions.

Figure S2 – 50 × 50 micron region contact mode atomic force microscopy topography (left) and friction (right) images in EtOH of 2,5,8,11-tetraoxatetradec-13-yne (TEG-alkyne) monolayers stamped onto azide-terminated silicon wafers. Topography image indicates a height of 1.0(1) nm. Friction image indicates the TEG-alkyne-terminated regions exhibit higher friction than the unreacted (azide-terminated) regions.

stamp for 30 sec before being removed from the stamp under a stream of N₂. The stamp was placed immediately onto an azide-terminated silicon wafer piece for at least 1 h. The stamp was then removed from the silicon wafer piece which was rinsed liberally in EtOH, followed by deionized H₂O, and then dried under a stream of N₂ and stored in a fluoroware container, protected from heat and light. **Figures S1–S3** show AFM images (topography and friction) of typical features prepared by microcontact printing the three compounds used in this communication: 4-pentynoic acid, propargylamine, and 2,5,8,11-tetraoxatetradec-13-yne (TEG-alkyne). Analysis of microcontact printed films by contact mode AFM indicated that the carboxylic acid terminated regions were approximately 1 nm taller than unreacted azide-terminated regions.

Direct-Write Click Chemistry of Propargylamine and TEG-Alkyne. Writing of alkynes onto azide surfaces was also possible with propargylamine and TEG-alkyne (**Figures S4–S5**) under the same conditions used to write 4-pentynoic acid.

Control Experiments. Attempts to reproduce direct-write click chemistry using SiN AFM tips on azide-terminated surfaces in 50 mM 4-pentynoic acid in EtOH failed. A constant scan rate of 2 $\mu\text{m/s}$ for *writing* at forces <400 nN failed to produce any raised features of higher friction. *Writing* with a force ~ 400 nN appeared to perturb the monolayer, possibly because of monolayer destruction.^{S2} Control experiments involving a copper AFM tip and 50 mM of ethanolic alkyne (4-pentynoic acid) on an azide-terminated surface produced similar results, confirming that both alkyne and a copper AFM tip are required to pattern an azide surface using this method. The contact mode topography and friction images shown in **Figure S6** – taken after attempting to write TEG-alkyne onto an azide surfaces using an *unmodified* SiN AFM tip – are representative of the results of these control experiments.

Materials. All reagents were obtained from commercial sources and were used as received. For AFM experiments we used 100% EtOH (Chromasolv, Sigma-Aldrich) and silicon-nitride AFM tips (DNP-S; Veeco Instruments, Woodbury, NY) with nominal tip radii of 10 nm and force constants ranging from 0.5 – 1 N/m. 2,5,8,11-Tetraoxatetradec-13-yne was prepared using a previously described procedure.^{S3}

AFM. All AFM work was performed on a Bioscope II (Veeco Instruments, Woodbury, NY) at the NUANCE Center at Northwestern University. All AFM imaging was done in contact mode. All images were subject to standard image processing protocols, including image flattening and contrast enhancement.

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