Electronic Supplementary Information

Mild Methods to Assemble and Pattern Organic Monolayers on Hydrogen-Terminated Si(111)

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Materials. Distilled water, 1-octadecene (90%), hexane, 2,2,6,6-tetramethyl-1-piperidinylxoy (TEMPO, 98%), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy, pentadecafluoro-octanoyl chloride (97%), undecanoic acid (99%), oxalyl chloride (98%), Al₂O₃ (basic, Brockman activity 1), 2-hexyldecanoic acid, 4-(dimethylamino)pyridine (99%), and 48% hydrofluoric acid were purchased from Acros or Aldrich and used as received. 40% NH₄F was purchased from J.T. Baker and used as received. All solvents were purchased from Acros and used as received. Geduran silica gel 60 was purchased from Fisher and used for all purifications. Single-side polished Si(111) wafers (n-type) were purchased from Silicon Inc, Boise, Idaho.

TEMPO was sublimed under reduced atmosphere, dried under vacuum for 48 h, and stored in a -30 °C freezer in a glove box under N₂. 1-Octadecene was distilled with a Vigreux column under reduced pressure. Typically 500 mL were distilled at one time. The first 100 mL of distilled 1-octadecene was discarded. We collected the next 300 mL of 1-octadecene and transferred it to a Kontes flask. The Kontes flask was evacuated under reduced pressure and back filled with N₂, this process was repeated three times. The Kontes flask was stored in the glove box.

NMR Instrumentation. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker DPX 300 using CDCl₃. The solvent signal was used as an internal standard. Trifluorotoluene (C₆H₅CF₃) was used as an internal standard for the ¹⁹F NMR.

Preparation of the Si(111)-H Surface and Assembly of the Monolayers. We will describe the steps to assemble monolayers on the Si(111) shards. All monolayers were assembled for 24 hours at room temperature. The concentrations of TEMPO and the derivatives of TEMPO in 1-octadecene were outlined in Table 1. The 1-octadecene, TEMPO, and derivatives of TEMPO were stored in a glove box and all preparations involving these chemicals were done inside of a glove box.

Shards of Si(111) wafers were cut into sizes of approximately 1 cm by 2.5 cm. These shards were washed with hexanes, acetone, and methanol and then sonicated in acetone for 5 min. The shards were rinsed with water and treated with 5:1 (v/v) 40% NH₄F(aq)/48% HF(aq) for 30 sec to remove the native silicon dioxide layer. The samples were placed in 3:1 (v/v) concentrated H₂SO₄/30%H₂O₂(aq) (piranha) for 1 h at 90 °C. Piranha is exceedingly dangerous
and should be kept from organic materials and treated with care. The wafers were removed from the piranha and washed with copious amounts of water. The wafers were hydrophilic after this treatment.

The 40% NH$_4$F was placed in a cup within a larger cup that was covered with a cap. The NH$_4$F was purged with Ar for 30 minutes to remove O$_2$ before the Si(111) shards were immersed. The larger cup was continuously purged with Ar while the Si(111) shards were immersed in the NH$_4$F for 20 min. The shards were removed and the NH$_4$F spontaneously dewetted from the surface. The shards were dried under a stream of N$_2$.

The shards were immediately taken into the glove box as is and immersed in the solution of 1-octadecene with TEMPO or derivatives of TEMPO according to Table 1. It is important to transfer the silicon shards into a glove box immediately after forming the hydrogen terminated surface as it rapidly oxidizes to silicon dioxide. The monolayers were assembled at room temperature in a sealed schlenk flask under N$_2$ for 24 h. After 24 h the shards were removed and washed with copious amounts of hexane, acetone, and methanol. Finally, the shards were sonicated twice for 3 min in CH$_2$Cl$_2$. New CH$_2$Cl$_2$ was used for each sonication. The contact angles were immediately measured on their surfaces.

For entries 14 and 15 in Table 1 the monolayers were assembled in neat hexane. Hexane was added to a Kontes flask and taken through four freeze-pump-thaw cycles. The hexane was transferred into the glove box and passed over Al$_2$O$_3$ that was activated in a 125 °C oven overnight. The hexane was collected and stored in a Kontes flask until use.

**Contact Angle Goniometry.** Contact angles were measured on a Ramé-Hart model 100 goniometer at room temperature and ambient humidity. An Eppendorf EDOS 5222 was used to dispense distilled water. Small drops of water (5 µL) were dispensed at a time and the contact angles were measured immediately. A minimum of 15 measurements at two different spots on the surface were collected for each sample. The error in the measurements of the advancing contact angles were typically small; for contact angles of greater than 100° most of the measurements came within ±1 of the reported value. Contact angles less than 100° had errors of ±2.

**X-ray Photoelectron Spectroscopy (XPS).** The XPS was done at the University of Illinois at the Center for Microanalysis of Materials (CMM) with the help of Rick Haasch. The instrument was a Kratos axis ultra X-Ray photoelectron spectrometer. The image area was 300 by 700 µm and the take-off angle was 90°. The pass energy on the survey scan (0 to 1100 eV) was 160 eV. High resolution scans of the Si(2p) (92 to 108 eV binding energy), C(1s) (274 to 300 eV binding energy), O(1s) (523 to 539 eV binding energy), and F(1s) (680 to 696 eV binding energy) were performed. The atomic compositions reported in Table 1 were corrected for the atomic sensitivities and measured from the high resolution scans. The atomic sensitivities were 1.000 for F(1s), 0.780 for O(1s), 0.278 for C(1s), and 0.328 for Si(2p).

**Synthesis of TEMPO-F$_{15}$.** 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (1.33 g, 7.7 mmol) was added to a schlenk flask. The flask was evacuated under reduced pressure and backfilled with N$_2$ three times. Methylene chloride (40 mL) and 4-(dimethylamino)pyridine (1.41 g, 11.55 mmol) were added to the flask under positive N$_2$ pressure. Pentadecafluorooctanoyl chloride (4.0 g, 9.3 mmol) was added and the reaction was stirred for 10 h. The reaction was extracted with 50 mL H$_2$O/10 mL concentrated HCl twice and with 50
mL H₂O twice. The product was rotovapped to a red solid. The product was cleaned by column chromatography in 5% ethyl acetate/hexanes. A red solid was isolated (3.00 g, 68% yield), evacuated under reduced pressure for 24 h, and stored in a -30 ºC freezer in a glove box. Phenyl hydrazine was added to the NMR tube. ¹H NMR (CDCl₃): δ 1.12 (s, 3H), 1.13 (s, 3H), 1.61 (t, J = 11.4 Hz, 2H), 1.89 (m, 2H), 5.18 (t of t, J = 11.4 Hz and 4.5 Hz, 1H). ¹⁹F NMR (CDCl₃ with C₆H₅CF₃): δ -80.36 (t of t, J = 2.7 Hz and 10.5 Hz, 3F), -118.15 (t of t, J = 2.7 Hz and 13.2 Hz, 2F), -121.22 (m, 2F), -121.63 (m, 2F), -122.01 (m, 2F), -122.33 (m, 2F), -125.68 (m, 2F). HRMS: Calculated for C₁₇H₁₇NO₃F₁₅: 568.0969. Found: 568.0969.

Synthesis of TEMPO-C₁₀. Undecanoic acid (3.24 g, 17.4 mmol) was added to a schlenk flask. The flask was evacuated under vacuum and backfilled with N₂ three times. Methylene chloride (30 ml) was added to the flask under positive N₂ pressure. The flask was cooled in an ice bath for 15 min. Oxalyl chloride (6.64 g, 52.3 mmol) was added to the flask. The flask was removed from the ice bath and warmed to room temperature. After 5 h the reaction mixture was rotovapped to remove the methylene chloride and excess oxalyl chloride. 4-Hydroxy-2,2,6,6-tetramethylpiperidinoxyl (2.5 g, 14.5 mmol), pyridine (2.3 g, 27.5 mmol), and methylene chloride (30 ml) were added to a schlenk flask under positive N₂ pressure and cooled in an ice bath. The acid chloride was added, and the reaction was allowed to stir at room temperature for 18.5 h. The reaction was extracted with 40 mL water five times. The organic layer was collected and the solvent was removed by reduced pressure to give a red crystalline product. The product was then purified by column chromatography in 8% ethyl acetate/hexanes. A red solid (3.85 g, 78.1% yield) resulted. Phenyl hydrazine was added to the NMR tube. ¹H NMR (CDCl₃): δ 0.75 (t, J = 7.5 Hz, 3H), 0.98-1.28 (m, 26H), 1.52 (m, 4H), 1.82 (m, 2H), 2.20 (t, J = 12.0 Hz, 2H), 5.00 (t of t, J = 12.0 Hz and 4.5 Hz, 1H). ¹³C NMR δ: 13.96, 20.37, 22.51, 24.81, 28.94, 29.10, 29.14, 29.30, 29.39, 31.74, 34.39, 43.75, 59.16, 66.29, 173.22. HRMS: Calculated for C₂₀H₃₈NO₃: 340.2852. Found: 340.2859.

Synthesis of TEMPO-C₆C₈. 2-Hexyldecanoic acid (1.95 g, 10.45 mmol) was added to a schlenk flask. The flask was evacuated under vacuum and backfilled with N₂ three times. Methylene chloride (30 ml) was added to the flask under positive N₂ pressure. The flask was cooled in an ice bath for 15 min. Oxalyl chloride (3.98 g, 31.4 mmol) was added to the flask. The flask was removed from the ice bath and warmed to room temperature. After 9 h the reaction mixture was rotovapped to remove the methylene chloride and excess oxalyl chloride. 4-Hydroxy-2,2,6,6-tetramethylpiperidinoxyl (1.5 g, 8.71 mmol), pyridine (1.38 g, 27.5 mmol), and methylene chloride (25 ml) were added to a schlenk flask under positive N₂ pressure and cooled in an ice bath. The acid chloride was added, and the reaction was allowed to stir at room temperature for 9 h. The reaction was extracted with 20 mL water five times. The organic layer was collected and the solvent was removed by reduced pressure to give a red crystalline product. The product was then purified by column chromatography in 8% ethyl acetate/hexanes. A red liquid (2.68 g, 74.5% yield) was recovered. Phenyl hydrazine was added to the NMR tube. ¹H NMR (CDCl₃): δ 0.77 (t, J = 7.5 Hz, 6H), 1.05-1.25 (m, 32H), 1.25-1.38 (m, 2H), 1.38-1.72 (m, 4H), 1.82 (m, 2H), 2.16 (m, 1H), 5.00 (t of t, J = 12.0 Hz and 4.5 Hz, 1H). ¹³C NMR δ: 14.06, 14.10, 20.54, 22.56, 22.65, 27.34, 27.37, 29.16, 29.21, 29.40, 29.50, 31.65, 31.83, 31.99, 32.50, 44.08, 45.80, 59.00, 66.28, 176.16. HRMS: Calculated for C₂₅H₄₈NO₃: 410.3634. Found: 410.3633.
Representative Examples of XPS Spectra. We show two representative examples of survey and high resolution scans of the XPS spectra summarized in Table 1. The first spectra are from SAMs assembled from 0.1 mole % TEMPO in 1-octadecene (entry 3 in Table 1 of the main text). We show the survey scan and then the high resolution scans of Si(2p) (92 to 108 eV), C(1s) (274 to 300 eV), O(1s) (523 to 539 eV), and F(1s) (680 to 696 eV).

The second spectra are from SAMs assembled from 0.1 mole % TEMPO-C_{10} in 1-octadecene (entry 11 in Table 1 of the main text). We show the survey scan and then the high resolution scans of Si(2p) (92 to 108 eV), C(1s) (274 to 300 eV), O(1s) (523 to 539 eV), and F(1s) (680 to 696 eV).
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