Supplemental Information

Potential Directed Assembly of Aryl Iodonium Salts onto Silicon {100} Hydride Terminated and Platinum Surfaces

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General synthetic procedures

Compound 1 was purchased from Aldrich Chemical Company. Compounds 2-5 were prepared according to the procedures listed below. All reactions were carried out under a dry argon atmosphere unless noted. ¹H NMR was carried out on a 400 MHz Bruker model DRX400. Proton chemical shifts (δ) are reported relative to the 7.24 ppm peak in CDCl₃ or the 3.1 ppm quintet peaks in CD₃CN. ¹³C NMR was carried out on a 100 MHz Bruker model DRX400. All peaks are reported relative to the 77.0 ppm peaks of CDCl₃ or the 39.5 ppm peaks of DMSO. FT-IR was carried out on a Perkin Elmer model system 2000. Methylene chloride, diethyl ether, THF, and acetonitrile were purchased as Sure/Seal™ bottles from Aldrich. 4-Trifluormethylphenylboronic acid, Triflic acid and 4-trifluoromethylaniline were purchased from Aldrich. Diacetoxybenzene, t-butylnitrite, boron trifluoride etherate and nitrosonium tetrafluoroborate were purchased from Acros. Potassium bromide was purchased from Perkin Elmer. Diacetoxyiodotrifluoromethylbenzene was prepared according to the procedure of Leffler.¹

Phenyl-(4-trifluoromethyl-phenyl)-iodonium; bromide (2).

The procedure of Carroll² was followed by adding dropwise trifluoromethanesulfonic acid (0.4 mL, 4 mmols) to a solution of diacetoxyiodobenzene (0.6 g, 2 mmols) dissolved in methylene chloride (20 mL) held at -30 ºC. After 30 min the solution was warmed to room temperature and held for 1 hour. The solution was recooled to -30 ºC and 4-trifluoromethylphenylboronic acid (0.4, 4 mmols) and the resulting solution was allowed to warm to room temperature overnight. The solvent was removed in vacuo to yield crude product. The iodonium salt was further purified by adding DI water (10 mL) and extracting with ether (10 mL). The salt was isolated as the bromide salt by precipitating with a potassium bromide (3 g) dissolved in DI water (10 mL) to yield 0.3 g (30%) of a light brown solid. IR (KBr) 2423.5, 3047.0, 1594.2, 1566.9, 1469.9, 1438.5, 1395.5, 1323.6, 1170.8, 1126.7, 1103.3, 1067.0, 1048.2, 1001.7, 991.6, 823.0, 771.7, 744.3, 732.5, 718.8, 678.8, 650.9, 589.0, 493.3, 475.8, 455.0, 418.7 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 7.72 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 7.6 Hz, 2 H), 7.16 (d, J = 8.4 Hz, 2H), 7.02 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.6 Hz, 2 H). ¹³C NMR
(100 MHz, DMSO) δ 135.6, 135.0, 131.4, 131.2, 130.9, 217.8(q), 125.3, 124.9, 122.2, 120.9.

**Trifluoro-methanesulfonatebis-(4-trifluoromethyl-phenyl)-iodonium; (3).**

The procedure of Carroll² was followed by adding dropwise trifluoromethanesulfonic acid (0.4 mL, 4 mmols) to a solution of 4-diacetoxyiodotrifluoromethylbenzene (0.8 g, 2 mmols) dissolved in methylene chloride (20 mL) held at -30 °C. After 30 min the solution was warmed to room temperature and held for 1 hour. The solution was recooled to -30 °C and 4-trifluormethylphenylboronic acid (0.4, 4 mmols) and the resulting solution was allowed to warm to room temperature overnight. The solvent was removed in vacuo to yield 0.2 g (15%) of pale brown product. IR (KBr) 3526.0, 3101.6, 1936.3, 1596.7, 1402.8, 1332.4, 1263.0, 1247.0, 1170.0, 1133.9, 1106.6, 1068.5, 1049.1, 1024.5, 995.8, 831.8, 771.5, 718.3, 682.9, 640.4, 589.2, 575.1, 517.6, 491.4 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 8.27 (d, J = 8.4 Hz, 4 H), 7.82 (d, J = 8.4 Hz, 4H). ¹³C NMR (100 MHz, CD₃CN) δ 136.0, 133.5 (q, J = 30 Hz), 128.6 (q, J = 3 Hz), 122.9 (q, J = 270 Hz), 122.0, 118.8.

**(4-Hexyloxy-phenyl)-phenyl-iodonium; bromide (4).**

The procedure of Crivello³ was followed except hexyloxybenzene was used instead of anisole to form the desired compound.

**4-Trifluoromethyl-benzenediazonium; tetrafluoro borate (5).⁴**

Boron trifluoride etherate (3.3 mL, 13 mmols) and THF (2.0 mL) were added to a 100 mL round bottom flask equipped with a stirbar and cooled to -30 °C. To the THF solution was added dropwise a solution of 4-Trifluomethylaniline (0.77 g, 6.6 mmols) dissolved in THF (4.0 mL). t-Butynitrite (1.2 mL, 9.9 mmols) dissolved in THF (2.0 mL) was added dropwise. After 30 min. at -30 °C the solution was allowed to warm to 0 °C and ether (50 mL) was added and the precipitate collected to yield 1.7 g (100%) of the desired product. ¹H NMR (400 MHz, CD₃CN) δ 8.70 (dd, J = 11.2, 2.4 Hz, 2 H), 8.21 (dd, J = 11.2, 2.0 Hz, 2H).

**General iodonium salt assembly procedure**

A 1.0 mmol/L solution of the iodonium salt was prepared by dissolving the iodonium salt into 0.1 mol/L solution of tetrabutylammonium tetrafluoroborate dissolved in acetonitrile. The freshly prepared silicon hydride substrate was connected to the negative terminal of a voltage source via a micro-alligator clip. The positive terminal of the voltage source was connected to a platinum wire. Both the substrate and the Pt wire were immersed into the iodonium solution and the voltage supply (-2V or -5V) was turned on. The assembly progresses for the desired length of time, the voltage was turned off, the substrate was sonicated in fresh acetonitrile for 30 seconds, rinsed with ethanol and dried under a stream of nitrogen.
**General diazonium salt assembly procedure**

A 1.0 mmol/L solution of the diazonium salt was prepared by dissolving the diazonium salt in acetonitrile. The freshly prepared silicon hydride substrate was incubated for the desired length of time, removed from the acetonitrile solution and washed with acetonitrile (3×) and dried using Ultrajet.

**Secondary ion mass spectroscopy experiments**

Patterns were created using As ion implantation at a dose of 2e15 As atoms/cm² at and 50 KeV. A 4-perfluorooctylbenzene diazonium; tetrafluoroborate diazonium salt was assembled according the before mentioned procedure on the implanted substrates. After assembly the substrates were characterized by TOF-SIMS analysis (Data acquired on a PHI TRIFT I TOF-SIMS. Primary ion: 25kV, 600pA 69Ga, in unbunched mode with no charge compensation. The data acquired over 140x140µm raster for 5 minutes per acquisition in both positive and negative secondary ion modes. The data was then analyzed using Sandia National Laboratory’s AXSIA multivariate analysis toolkit.) The diazonium salt assembled onto the entire substrate with enhanced assembly (~1.5×) with the doped regions as shown below.

![A photo of the implanted substrate.](image)

![TOF-SIMS spectra for Positive Ions: Red: Fluorocarbons, Blue: H-terminated Silicon, Green: Fluorocarbons, Yellow: silicones.](image)

**XPS data acquisition and analysis**

X-ray Photoelectron Spectroscopy (XPS) was used to confirm the assembly of the iodonium salts on silicon hydride terminated substrates. XPS spectra were acquired on a Kratos Axis Ultra X-ray photoelectron Spectrometer using a monochromatic Al Kα source operating at 300 W, and charge compensation using low energy electrons. Survey, high resolution and valence band (VB) spectra were acquired at pass energies of 80 eV, 20 eV, and 40 eV respectively. Hybrid magnification mode was used for the highest sensitivity analysis with the x-ray monochromator. This magnification gives an analysis area of approximately 700 micron by 300 micron. Acquisition time per spectra was 2
minutes for survey spectra, 1.5 - 60 minutes for high resolution spectra, and 10 minutes for valence band spectra. For Angle Resolved XPS (ARXPS) the acquisition time was increased. Data analysis and quantification were performed using the Vision software provided by the manufacturer and CasaXPS software. Sensitivity factors were provided by manufacturer. A linear background subtraction was used for curve fitting of high resolution spectra.

References